THE SYNTHESIS and STUDY

of

POLYCYCLIC AROMATIC HYDROCARBONS.

T H E S I S

presented by

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for the degree of

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ACKNOWLEDGMENTS.

I wish to record my grateful thanks to Dr. E. Clar for his attentiveness, guidance and encouragement throughout the course of this work.

I would also like to thank Dr. M. Zander for a gift of 2.8 - di (o - carboxylbenzyl) - chrysene and for recording the phosphorescence spectrum of 1.2, 3.4, 5.6, 7.8, 9.10, 11.12 - hexabenzocoronene.

My thanks are also recorded to the Department of Scientific and Industrial Research for a subsistence allowance, and to Mr. J.M.L. Cameron and his staff who carried out micro-analyses.

Finally, I would like to thank Mr. H. Hunter who was associated with me in the work outlined in Chapters IV and VI.

PUBLICATIONS.

The following papers have been or are about to be published:

1. Annellation Effects in the Fluoranthene Series.

   E. Clar and J.F. Stephen.

   Tetrahedron, 20, 1559 (1964).

2. Higher Annellated 1.2, 7.8 - Dibenzochrysenes.

   E. Clar, J.F. Guye-Vuilleme and J.F. Stephen.

   Tetrahedron, 20, 2107 (1964).

3. The Synthesis of 1.2, 3.4, 5.6, 7.8, 9.10, 11.12 - Hexabenzocoronene.

   E. Clar and J.F. Stephen.

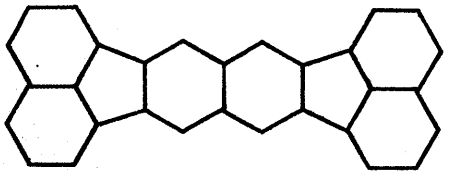
   Tetrahedron, in press.

-------oOo-------

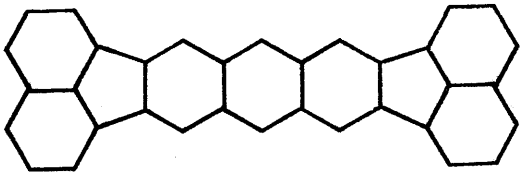
C O N T E N T S

SUMMARY

Di - 2.3, 6.7 - (peri - naphthylene) - naphthalene (I) and di - 2.3, 6.7 - (peri-naphthylene) - anthracene (II) were synthesised. From a study of the asymmetric annellation effects which are observed when two peri - naphthylene complexes are connected to benzene, naphthalene and anthracene, it has been concluded firstly, that during one of the annellations leading to a di - (peri - naphthylene)-acene the aromatic system of the central acene is extended to a system with two more rings, for example the aromatic system of benzene is extended to an anthracene system, and secondly, in the di - (peri - naphthylene) - acenes which are formally symmetric molecules there is an asymmetric distribution of $\overline{\Pi}$ - electrons.



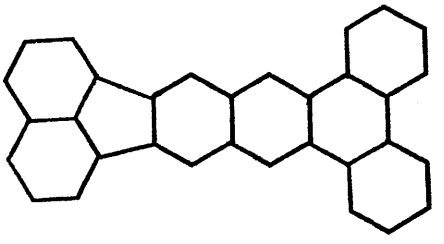
I



II

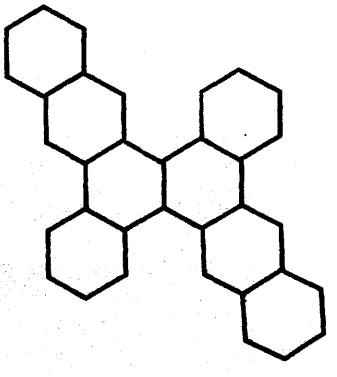
The asymmetric hydrocarbon 1.2, 3.4 - dibenzo - 6.7 - (peri -

naphthylene) - anthracene (III) was prepared. The annellation effects observed in building up (III) from naphthalene indicate that the system in aromatic conjugation in (III) is the 11.12 - benzofluoranthene system.

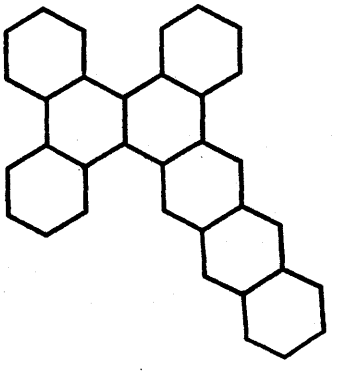


III

Tetrapheno - (6'.5' - 5.6) - tetraphene (IV) and 1.2 - benzo-phenanthreno - (9'.10' - 3.4) - tetracene (V) were prepared. Oxidation and annellation effect point to a fixed double bond in 1.2, 7.8 - dibenzo-chrysene. This is not so in the higher benzologues (IV) and (V) which are closely related to anthraceno - (2'.1' - 1.2) - anthracene and naphtho - (2'.1' - 1.2) - tetracene.

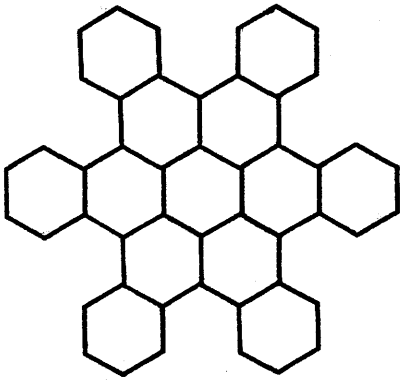


IV



V

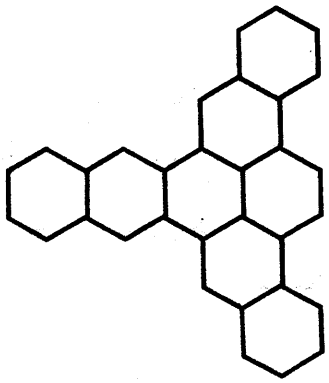
The synthesis of 1.2, 3.4, 5.6, 7.8, 9.10, 11.12 - Hexabenzo coronene (VI) has been achieved. As a hydrocarbon with six inherent sextets, (VI) shows an intense red phosphorescence at low temperature. The absorption spectrum of (VI) occurs at a shorter wavelength than would be expected from a consideration of the number of $\widetilde{\pi}$ - electrons in (VI) and this has been explained by assuming that only a fraction of the rings are in aromatic conjugation; both solubility and $\lambda_\alpha : \lambda_\beta$ ratio suggest that (VI) is not uniplanar.



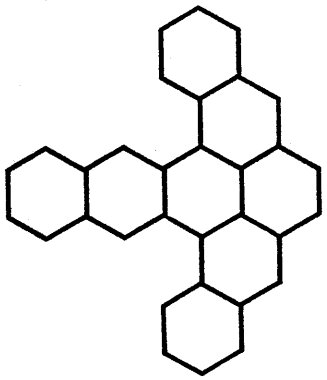
VI

The isomeric hydrocarbons 4.5, 8.9 - dibenzo - naphtho - (2'''.3''' - 1.2) - pyrene (VII) and 3.4, 9.10 - dibenzo - naphtho - (2'''.3''' - 1.2) - pyrene (VIII) were prepared and a comparative study of the effects of fusing one and two rings to the 1.2 and 6.7 double

bonds of 3.4, 9.10 - dibenzopyrene has been made.



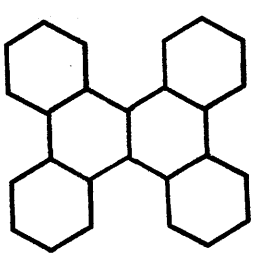
VII



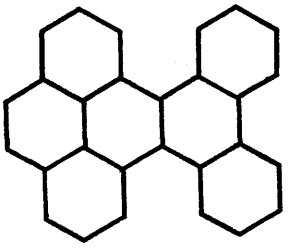
VIII

1.2, 7.8 - Dibenzochrysene (IX), phenanthreno - (9'.10' - 1.2) - pyrene (X) and pyreno - (1'.2' - 1.2) - pyrene (XI) were prepared by reducing fluorenone, a mixture of fluorenone and 4.5 - carbonylphenanthrene and 4.5 carbonylphenanthrene respectively in a zinc dust melt. It is suggested that the formation of 1.2, 7.8 - dibenzochrysene (IX) involves the dimerization of two molecules of fluorenone to 9.9' - dihydroxy - 9.9' bifluorenyl which then undergoes a pinacol - pinacolone rearrangement to 10.10 - diphenylene - 9 - phenanthrone. This ketone is then reduced to 10.10 - diphenylene - 9.10 - dihydro -

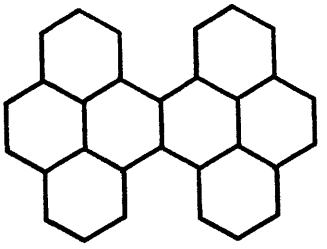
9 - phenanthrol which is converted to (IX) by retropinacolone rearrangement.



IX

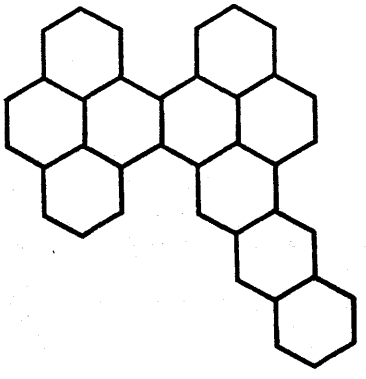


X



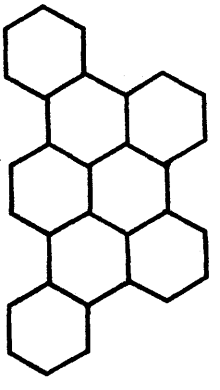
XI

Naphtho - (2''.3'' - 4.5) - pyreno - (1'.2' - 1.2) - pyrene (XII) was prepared from pyrenopyrene (XI). Its spectrum shows two sets of para - bands. The short wavelength group can be related to the non-annellated pyrene complex and the long wavelength group to the naphthopyrene complex in (XII).

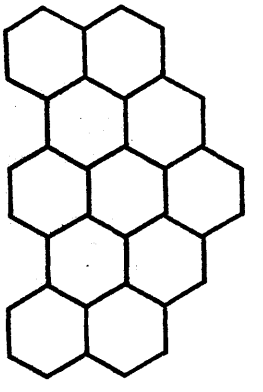


XII

3.4, 5.6, 7.8, 12.13 - Tetrabenzoperopyrene (XIV) was synthesised. (XIV) can be derived from the fully benzenoid 1.12, 2.3, 10.11 - tribenzoperylene (XIII) by fusing three ethylene bridges. The annellation effects passing from (XIII) to (XIV) indicate that the newly formed rings in (XIV) are empty.



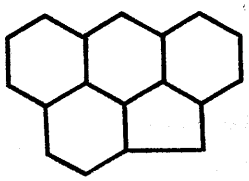
XIII



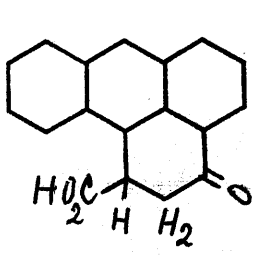
XIV

Two attempts to establish the naphtho - (7'.8' - 1.7) - acenaphthylene skeleton (XV), firstly by cyclizing the zinc, sodium hydroxide reduction product of 1.2 - dihydro - benzanthrone - (3) - 1 - carboxylic acid (XVI) with zinc chloride and secondly, by reducing 1H - benzanthrene - 1 - carboxylic acid (XVII) in a zinc dust melt were unsuccessful. The former reaction gave 1.10 - trimethylene-

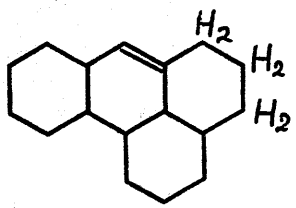
phenanthrene (XVIII), the latter 4.5, 11.12 - dibenzoperopyrene (XIX), decarboxylation having occurred in both cases.



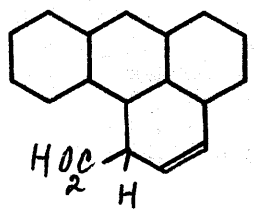
XV



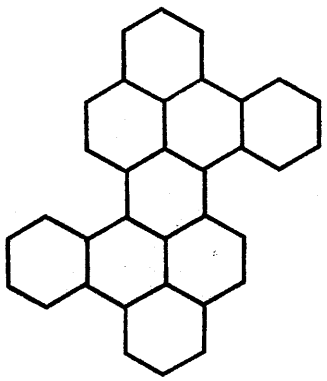
XVI



XVIII



XVII



XIX

N O M E N C L A T U R E.

The nomenclature used by E. Clar in his book "Polycyclic Hydrocarbons" is used throughout this thesis. Two symbols are used extensively a hexagon (I) and a hexagon with circle inscribed (II)

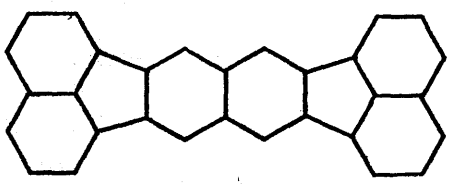
I.

II.

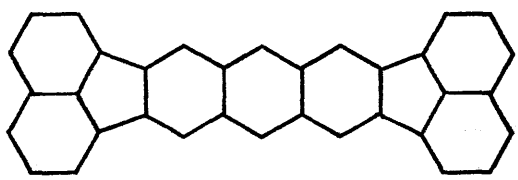
The former symbol represents an aromatic ring, the latter symbol - introduced by Sir R. Robinson - represents a benzenoid ring, a ring which possesses three conjugated double bonds, that is, 6 π - electrons in an "aromatic sextet".

CHAPTER I.

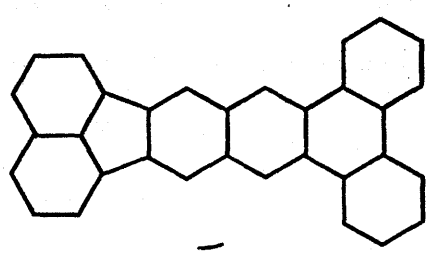
DI - 2.3, 6.7 - (peri - NAPHTHYLENE) - NAPHTHALENE,
DI - 2.3, 6.7 - (peri - NAPHTHYLENE) - ANTHRACENE and
1.2, 3.4 - DIBENZO - 6.7 - (peri - NAPHTHYLENE) - ANTHRACENE.



I



II



III

INTRODUCTION: From a study of the annellation effects observed when two o - diphenylene complexes are fused to an acene forming

firstly a 1.2, 3.4 - dibenzacene and then a symmetric tetrabenzacene Clar has shown[1,2] firstly, that during one of the annellations leading to a tetrabenzacene the central acene system is extended by one ring, for example, the aromatic system of benzene is extended to a naphthalene system and secondly, that in the tetrabenzacenes which are formally symmetric molecules there is an asymmetric distribution of $\overline{\pi}$ - electrons.

Hitherto no study has been made of the annellation effects which accompany the fusion of two peri-naphthylene complexes to an acene forming firstly a fluoranthene and then a symmetric di - (peri - naphthylene) - acene. The annellation of a peri-naphthylene complex differs from the annellation of an o - diphenylene complex in that while the latter annellation forms a six membered ring the former annellation results in the formation of a five membered ring. Hence any extension of conjugation which may result from the annellation of a peri-naphthylene complex must involve conjugation through a five membered ring. The object of the present work was to study this type of annellation. In the first series derived from benzene, benzene, fluoranthene and 11.12 - (peri - naphthylene) - fluoranthene[3] all three hydrocarbons are known. However to make possible a more comprehensive study of the annellation effects associated with the fusion of two peri-naphthylene complexes to an acene it was essential that the series derived from naphthalene, naphthalene, 11.12 - benzofluoranthene[4] and di - 2.3, 6.7 - (peri - naphthylene) - naphthalene and the series derived from anthracene, anthracene, naphtho (2'.3' - 11.12) - fluoranthene[5] and di - 2.3, 6.7 - (peri - naphthylene) - anthracene be completed. Di - 2.3, 6.7 - (peri - naphthylene) - naphthalene (I) and di - 2.3, 6.7 -

(peri - naphthylene) - anthracene (II) were therefore synthesised.

A third hydrocarbon, 1.2, 3.4 - dibenzo - 6.7 - (peri - naphthylene) - anthracene (III) was also prepared. This hydrocarbon is asymmetric and the central aromatic system has two possibilities of extending conjugation either by coupling with the o - diphenylene complex or by coupling with the peri-naphthylene complex. By studying the annellation effects which are recorded in passing from naphthalene to (III) it should be possible to say whether the central naphthalene system shows a preference for conjugating with the o - diphenylene or the peri-naphthylene complex.

THEORETICAL DISCUSSION: A systematic study of the absorption spectra of fluoranthene and its benzologues has been made and before discussing the effects of fusing two peri-naphthylene complexes to benzene, naphthalene and anthracene a short account of the classification of the absorption bands of aromatic hydrocarbons and the determination of the polarization of the absorption bands of fluoranthene, based on annellation effect will be given.

The regular appearance of three main band systems in the absorption spectra of hydrocarbons ranging from benzene to its very complex homologues containing fused rings was first pointed out by Clar in 1936.[6] These band systems retain their characteristic properties in the absorption spectra of different hydrocarbons and this fact makes a classification of band systems possible.[7] The band systems were classified as α, β and p - band systems and the criteria used for the classification were as follows:-

The position, intensity and polarization[8] of the bands. The

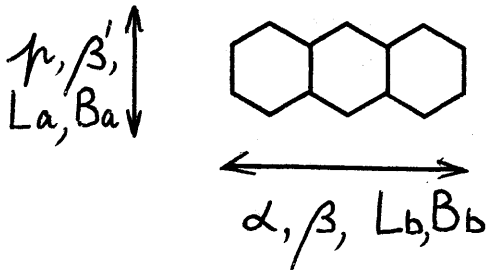
shifts in wavelength produced by annellation, the shifts observed in going from room temperature to -180° [9] and the shifts observed in passing from the gaseous to the liquid and solid states.[10]

Some characteristic features of the three band systems are summarized in Table I.

Table I - Classification of absorption bands

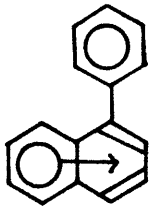
	α - Band	p - Band	β - Band
Extinction coef. log ϵ_{max}	2 - 3	4	4 - 6
Polarization, acene	longitudinal	transverse	longitudinal
Gas→Solution in hexane or alcohol.	250 cm^{-1}	900 cm^{-1}	900 cm^{-1}

In 1949 Platt[11] introduced a second classification of absorption bands, a classification based on molecular axes. The long molecular axis was termed a and the short axis b and the absorption bands were designated La, Ba, Lb, and Bb. In the acenes the La, Ba - bands are polarized transversely, that is across the width of the molecule and the Lb, Bb - bands are polarized longitudinally, along the length of the molecule.



The La, Ba, Lb and Bb - bands of the Platt classification may be identified with the p, β', α and β - bands respectively of the Clar classification. Since the annellation and molecular axes coincide in the acenes the only difference in the two classifications is one of nomenclature. However this is not so in angular and condensed hydrocarbons where considerable differences in the polarization of the absorption and fluorescence bands are observed.[12] These are so strong in perylene that the prediction of the polarization differs by 90° between the classification based on the molecular axes and the annellation axes, the latter giving the correct result.[13]

Let us now discuss the polarization of the absorption bands of fluoranthene. Only a small shift is observed in the β - band of naphthalene in passing from naphthalene to 1 - phenylnaphthalene (IV). The situation is very little altered by introducing the methylene group in benzanthrene (V) and in 3.4 - benzofluorene (VI). The shifts are 50, 70 and 100 A° respectively.[14] Even in perylene (VII) the two single bonds connecting the naphthalene complexes produce a shift of only 300 A° which



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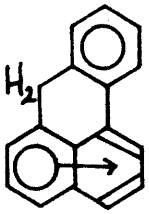

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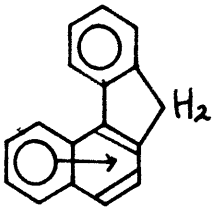

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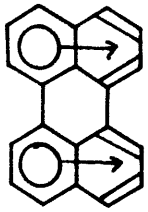
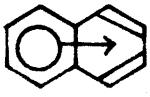
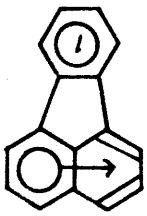


VII

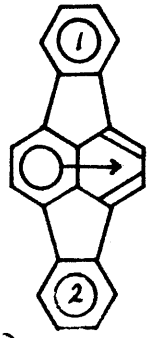
λ_β = 2260 2280 2310 2510 A°



VIII

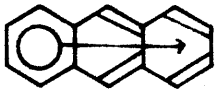


IX

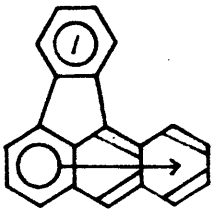


X

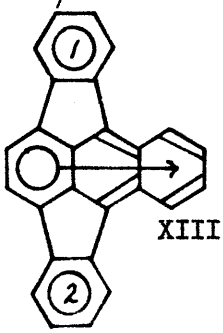
λ_β = 2210 $\xrightarrow{+150}$ λ_β' = 2360 (A) $\xrightarrow{+170}$ λ_β' = 2530 (A)



XI

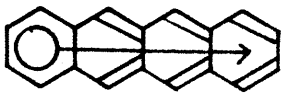


XII

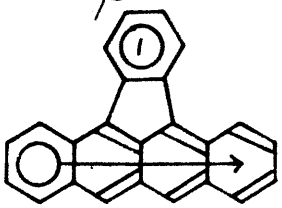


XIII

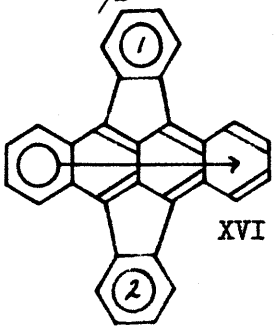
λ_β = 2515 $\xrightarrow{+45}$ λ_β' = 2560 (A) $\xrightarrow{+120}$ λ_β = 2680 (A)



XIV



XV



XVI

$\lambda_\beta = \begin{Bmatrix}2740\\2930\end{Bmatrix}$ $\xrightarrow{+60}$ λ_β' = 2925 (B) $\xrightarrow{+125}$ λ_β = 3050 (B)

Solvent: A = Alcohol, B = Benzene.

is hardly more than double the shift (145 A^{o}) in passing from benzene to diphenyl.

The absorption spectrum of fluoranthene (Figure I) shows two β - bands at 2870 and 2360 A^{o}. The latter, the β' - band is also very little affected by the successive fusion of the o - phenylene groups 1 and 2 to naphthalene forming fluoranthene (IX) and 4.5 - (peri - naphthylene) - fluoranthene (X).[15] The shifts are 150 and 170 A^{o} respectively. Similar small shifts of the β' - band (45 and 120 A^{o} respectively) are recorded for the connection of the o - phenylene groups 1 and 2 to anthracene (XI). In the series derived from tetracene the shifts are (60 and 125 A^{o} respectively). A shift of the fluoranthene β - band at 3870 A^{o} cannot be observed with certainty in the hydrocarbons derived from anthracene, (XIII)[16] and tetracene, (XVI).[17] Therefore it appears that the β' - band in (X) and the β - bands in (XIII) and (XVI) originate from polarization along the acene system, just as is the case in the acenes themselves.

The β - band of fluoranthene at 2870 A^{o} must be polarized perpendicular to the β' - band at 2360 A^{o} because it shifts strongly to the red if the o - phenylene ring in fluoranthene is annellated to give 11.12 - benzofluoranthene and naphtho - (2'.3' - 11.12) - fluoranthene. If the β - band of fluoranthene is polarized perpendicular to the β' - band then so also is the α - band, because the α and β - bands are interdependent and show a ratio of 1:1.35 similar to two Rydberg transitions. The remaining band the para - band must be polarized perpendicular to the α and β - bands, that is polarized along the naphthalene complex as is the β' - band.

Two different annellation series can be built up from benzene.

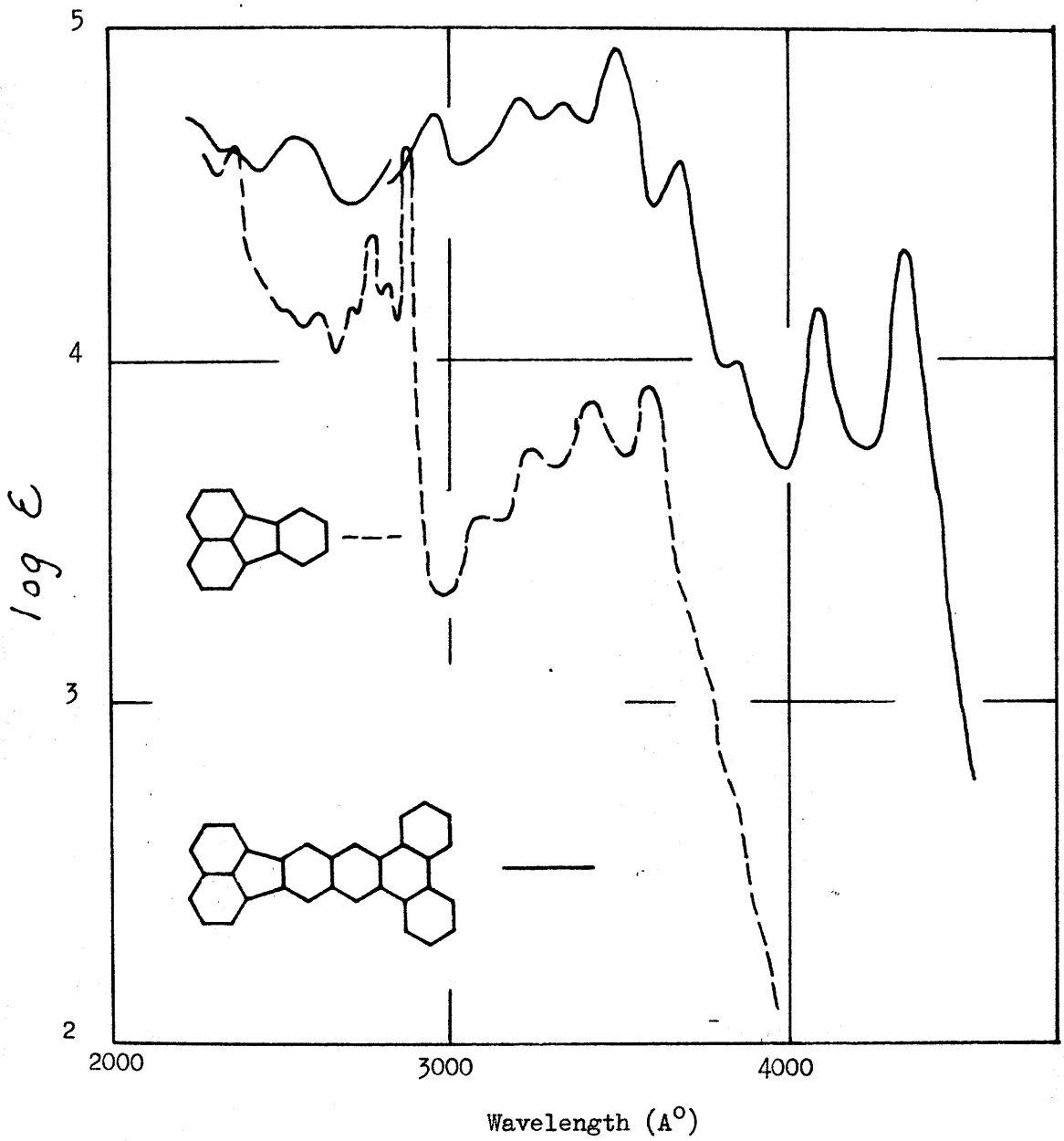
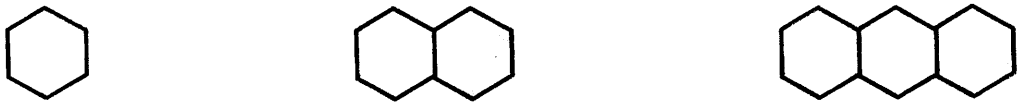


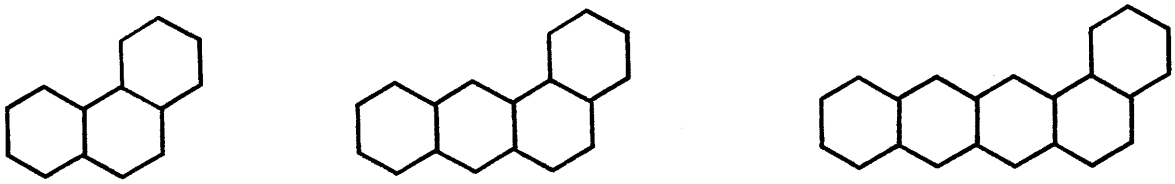
Figure 1. Absorption max. (A°) and log ε (in parentheses). Fluoranthene in ethanol, p: 3585 (3.95), 3420 (3.90), 3230 (3.76), 3090 (3.56); β : 2870 (4.66), 2820 (4.26), 2760 (4.40), 2715 (4.17), 2615 (4.16) 2525 (4.17); β': 2360 (4.66). 6.7 - (peri - naphthylene) - 1.2, 3.4 - dibenzanthracene in benzene, p: 4360 (4.31), 4100 (4.14), 3860 (4.00), 3690 (4.58); β : 3500 (4.92), 3340 (4.76), 3200 (4.78), 2950 (4.74); in cyclohexane, 2540 (4.66).

Linear annellation gives rise to the well known acene series, benzene, naphthalene, anthracene ...



λ_β = 1819 $\xrightarrow{+391}$ 2210 $\xrightarrow{+305}$ 2515 A°

Angular annellation gives rise to the phene series, phenanthrene, tetraphene, 1.2 - benzotetracene ...



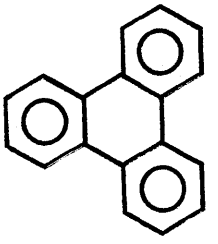
λ_β = 2510 $\xrightarrow{+360}$ 2870 $\xrightarrow{+290}$ 3190 A°

Constant spectral shifts accompany the fusion of each butadiene complex in both the above series.

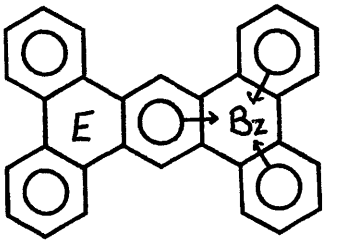
In striking contrast is the asymmetric annellation effect which accompanies the successive fusion of two o - diphenylene complexes to an acene.[1,2] For example, if we take benzene (XVII) and connect first one and then a second p - diphenylene complex we get triphenylene (XVIII) and the symmetric tetrabenzanthracene (XIX). The first shift is much greater than the second. These shifts are recorded in A° or better in $\sqrt{\text{A}^\circ}$ which is a scale for reciprocal nuclear charge.[18] In order to eliminate the influence

of the external rings the second shift XVIII ⟶ XIX in $\sqrt{\text{Å}}$ is subtracted from the β - band of triphenylene in $\sqrt{\text{A}^\circ}$.

XVII



XVIII



XIX

λ_β =	1819	+751 ⟶	2570	+355 ⟶	2925 A°
$\sqrt{\lambda_\beta}$ =	42.65	+8.05 ⟶	50.70	+3.40 ⟶	54.10 A°

$$50.70 - 3.40 = 47.30\sqrt{\text{Å}} = 2237 \text{ A}^\circ$$

$$\lambda_\beta \text{ naphthalene} = 2210 \text{ A}^\circ$$

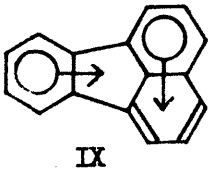
This gives a β - band at $47.30\sqrt{\text{Å}}$ or 2237 which is almost identical with the β - band of naphthalene which is 2210 Å in alcoholic solution. Thus during the course of one of the annellations the central aromatic system of benzene has been extended to a naphthalene system while the other annellation does not extend it to an anthracene system but produces an empty ring (E). It must therefore be concluded that each inherent benzenoid ring can transfer only 2 π - electrons to form an induced benzenoid ring (Bz). It appears that the formation of an induced benzenoid sextet has preference over a symmetric distribution of π - electrons. The same principle applies to the central acene system in the higher tetrabenzacenes.[1]

The annellation series acene, 1.2, 3.4 - dibenzacene and tetrabenzacene is only one of several asymmetric annellation series which have been studied. Others are the acene, 1.2 - benzacene and 1.2, 3.4 - dibenzacene series,[2] the series perylene, 1.12 - o - phenyleneperylene and 1.2, 7.8 - dibenzocoronene[19] and the series diphenyl, phenanthrene and pyrene.[20] In each series during one of the annellations an induced benzenoid ring is formed.

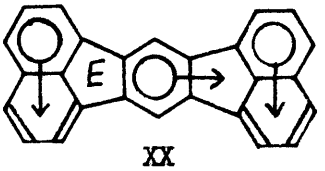
The annellation effects observed when two peri-naphthylene complexes are fused to benzene forming fluoranthene (IX) and 11.12 - (peri - naphthylene) - fluoranthene (XX) (Spectrum Figure II) are (1035 and 350 A^{o} respectively). If the shift for the second annellation in $\sqrt{A^{o}}$ is subtracted from the β - band of fluoranthene in $\sqrt{\text{Å}}$ a β - band at 50.39 $\sqrt{\text{Å}}$ corresponding to 2539 Å is obtained. This is almost identical to the β - band of anthracene or phenanthrene (2493 A^{o}) as calculated by the annellation principle.[18] An asymmetric aromatic conjugation which extends the aromatic system of benzene to a system with two more rings must have taken place.

The annellation of a peri-naphthylene complex to naphthalene brings about a big shift in passing to 11.12 - benzofluoranthene (XXI) and a smaller shift in going to di - 2.3, 6.7 - (peri - naphthylene) - naphthalene (I) (Spectrum Figure (III)). Deduction of the second shift in $\sqrt{\text{Å}}$ from the β - band of 11.12 - benzofluoranthene gives a β - band at 53.73 $\sqrt{A^{o}}$ or 2887 A^{o} which shows that the aromatic system of naphthalene has been extended by two rings.

In the next higher series, anthracene, naphtho - (2'.3' - 11.12) -



IX



XX

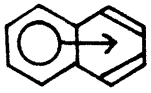
λ_β = 1835 $\xrightarrow{+1035}$ 2870 (A) $\xrightarrow{+350}$ 3220 (C)

$\sqrt{\lambda_\beta}$ = 42.84 $\xrightarrow{+10.73}$ 53.57 $\xrightarrow{+3.18}$ 56.75

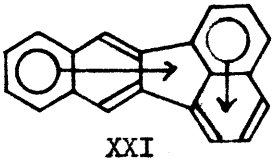
λ_p = 2068 (A) $\xrightarrow{+1517}$ 3585 (A) $\xrightarrow{+575}$ 4160 (C)

53.57 - 3.18 = 50.39 Å = 2539 A°

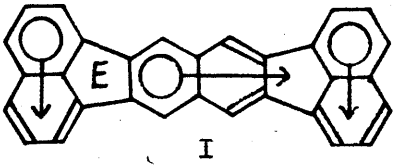
Calc. for 3 annellated rings 2493 A°



VIII



XXI



I

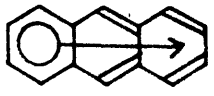
λ_β = 2210 (A) $\xrightarrow{+870}$ 3080 (A) $\xrightarrow{+200}$ 3280 (C)

$\sqrt{\lambda_\beta}$ = 47.01 $\xrightarrow{+8.49}$ 55.50 $\xrightarrow{+1.77}$ 57.27

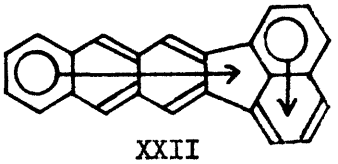
λ_p = 2850 (A) $\xrightarrow{+1150}$ 4000 (A) $\xrightarrow{+450}$ 4450 (B)

55.50 - 1.77 = 53.73 Å = 2887 A°

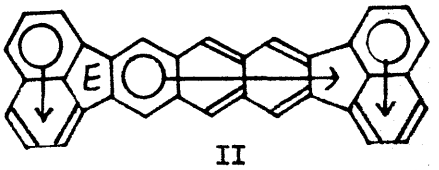
Calc. for 4 annellated rings 2803 A°



XI



XXII



II

λ_β = 2515 (A) $\xrightarrow{+825}$ 3340 (A) $\xrightarrow{+180}$ 3520 (C)

$\sqrt{\lambda_\beta}$ = 50.15 $\xrightarrow{+7.64}$ 57.79 $\xrightarrow{+1.54}$ 59.33

λ_p = 3745 (A) $\xrightarrow{+635}$ 4380 (A) $\xrightarrow{+350}$ 4730 (B)

57.79 - 1.54 = 56.25 Å = 3164 A°

Calc. for 5 annellated rings 3132 A°

Solvent: A = Alcohol, B = Benzene, C = Cyclohexane.

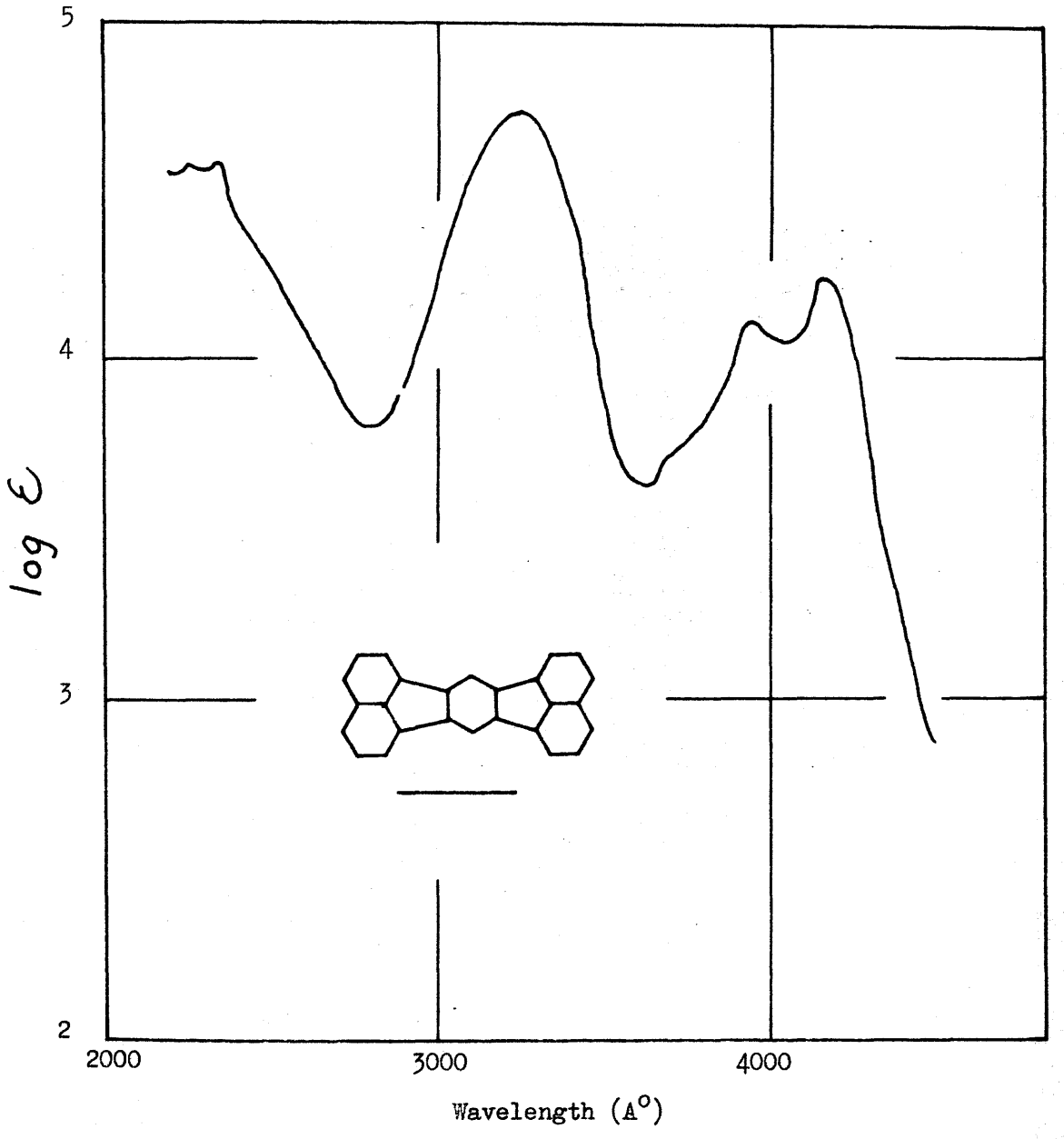


Figure 2. Absorption max. (A°) and log ε (in parentheses). 11.12 - (peri - naphthylene) - fluoranthene in benzene, p: 4170 (4.24), 3940 (4.10); β: 3250 (4.72); in cyclohexane, β': 2360 (4.58).

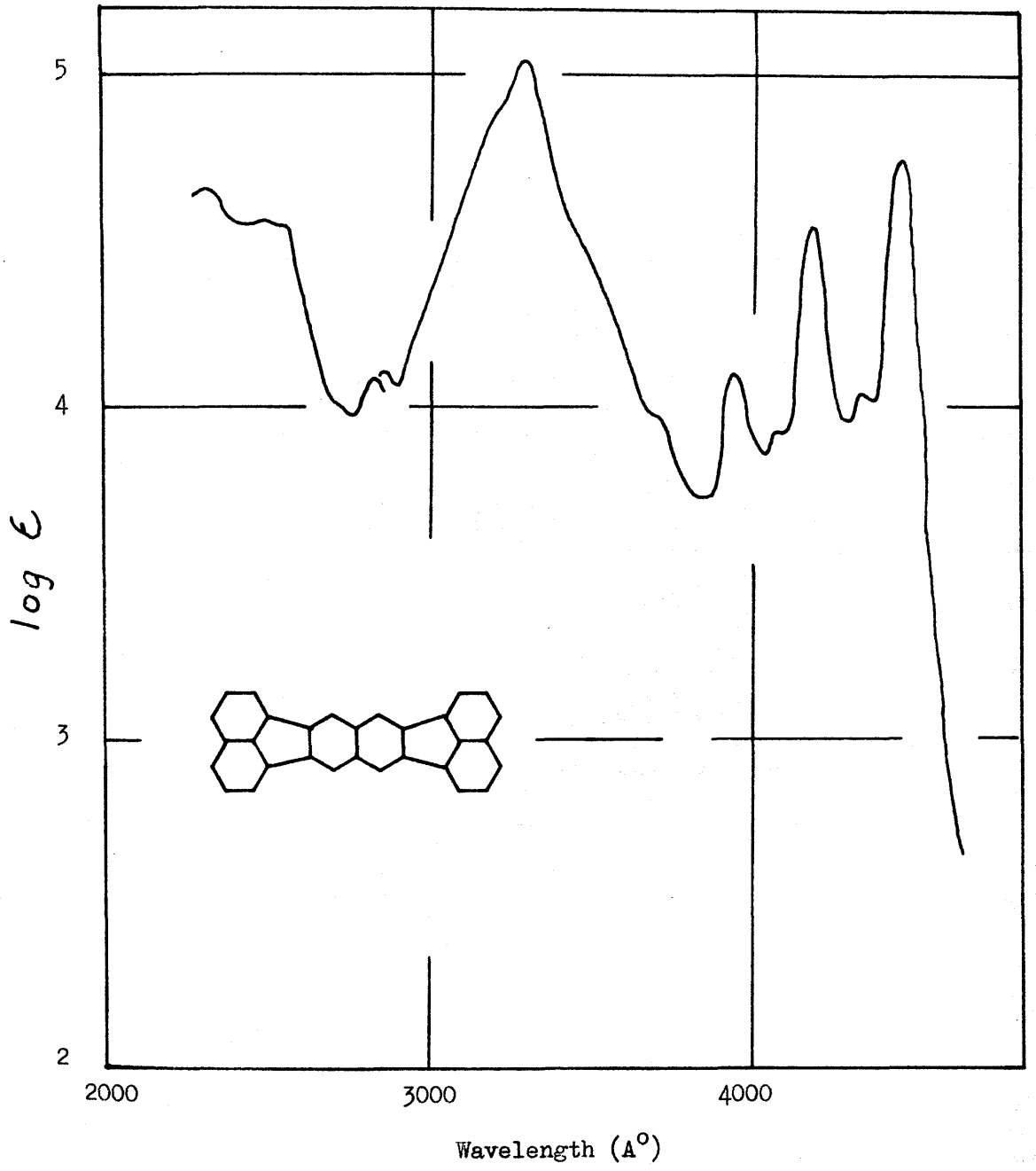


Figure 3. Absorption max. (A°) and log ε (in parentheses). 2.3, 6.7 - Di - (peri - naphthylene) - naphthalene in benzene, p: 4450 (4.74), 4180 (4.54), 3940 (4.09); β: 3290 (5.04), 2850 (4.10); in cyclohexane, β': 2320 (4.80).

fluoranthene (XXII) and di - 2.3, 6.7 - (peri - naphthylene) - anthracene (II) (Spectrum Figure IV) the annellation effect is again very asymmetric (895 and 180 A^{o}) and the shift subtraction rule, carried out in units of $\sqrt{\text{Å}}$, yields a β - band at 3164 A^{o} which indicates that the central anthracene system has been extended to a system with two more rings.

We have already seen that the successive fusion of two o - diphenylene complexes to an acene forming firstly a dibenzacene and then a tetrabenzacene is accompanied by an asymmetric annellation effect which indicates that the initial acene system has been extended by one ring. This is half the effect reported above and it shows that both rings of one peri - naphthylene complex participate in aromatic conjugation as indicated by the arrow and that the second annellation produces an empty ring (E). The η - bands also show very asymmetric annellation effects.

1.2, 3.4 - Dibenzo - 6.7 - (peri - naphthylene) - anthracene (III) (Spectrum Figure I) can be constructed from naphthalene by fusing an o - diphenylene and a peri-naphthylene complex. If the latter annellation can account for the extension of the aromatic system of naphthalene by two rings and the former annellation for only one then conjugation must exist between the two naphthalene complexes as indicated by the arrow and not between the central naphthalene system and the o - diphenylene system. There must be an empty ring (E). This can be shown by comparing the shifts observed when an o - diphenylene complex is fused to 11.12 - benzofluoranthene (XXI) to form 1.2, 3.4 - dibenzo - 6.7 - (peri - naphthylene) - anthracene (III) and the shift recorded in passing from 1.2, 3.4 - dibenzanthracene

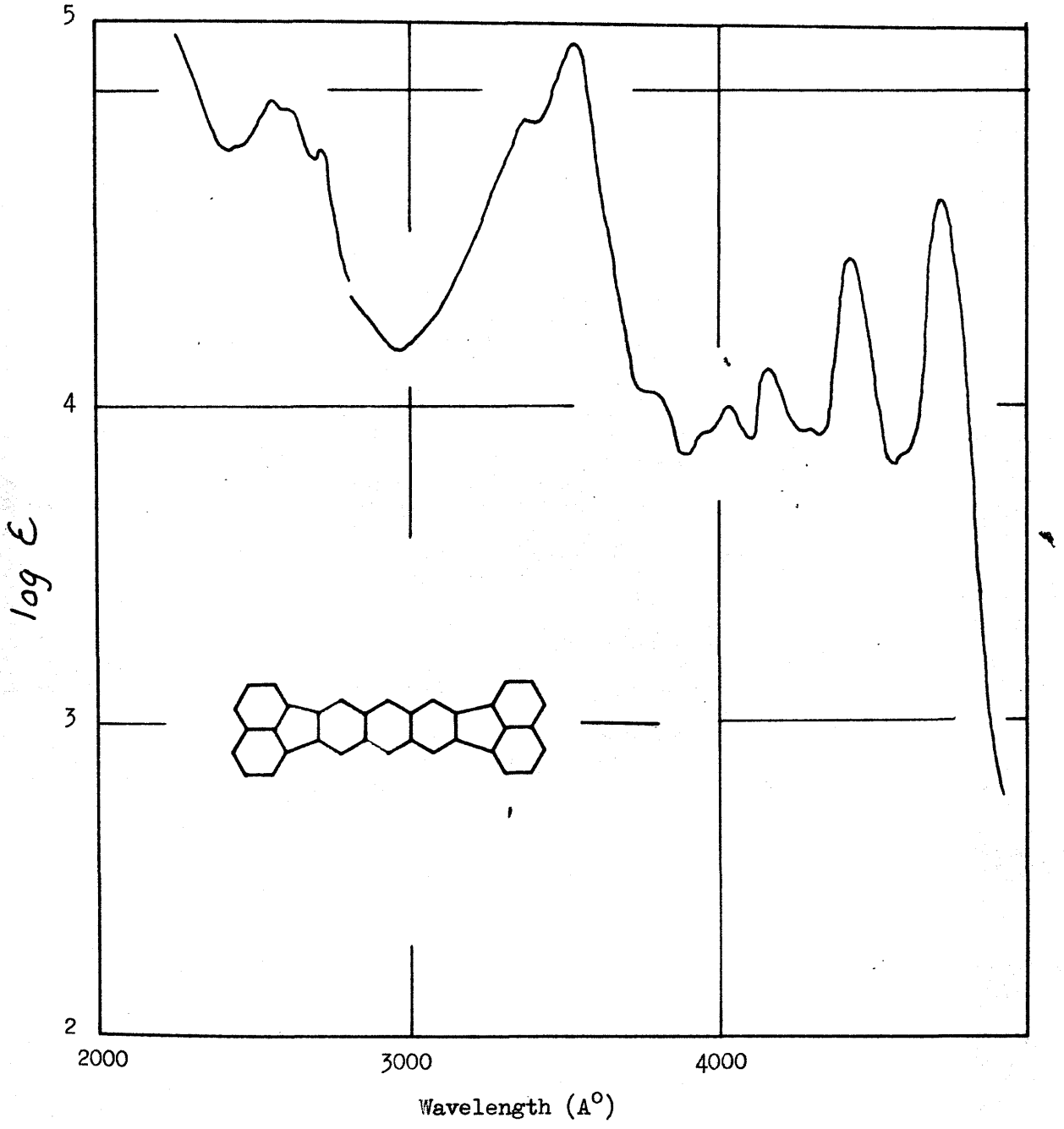
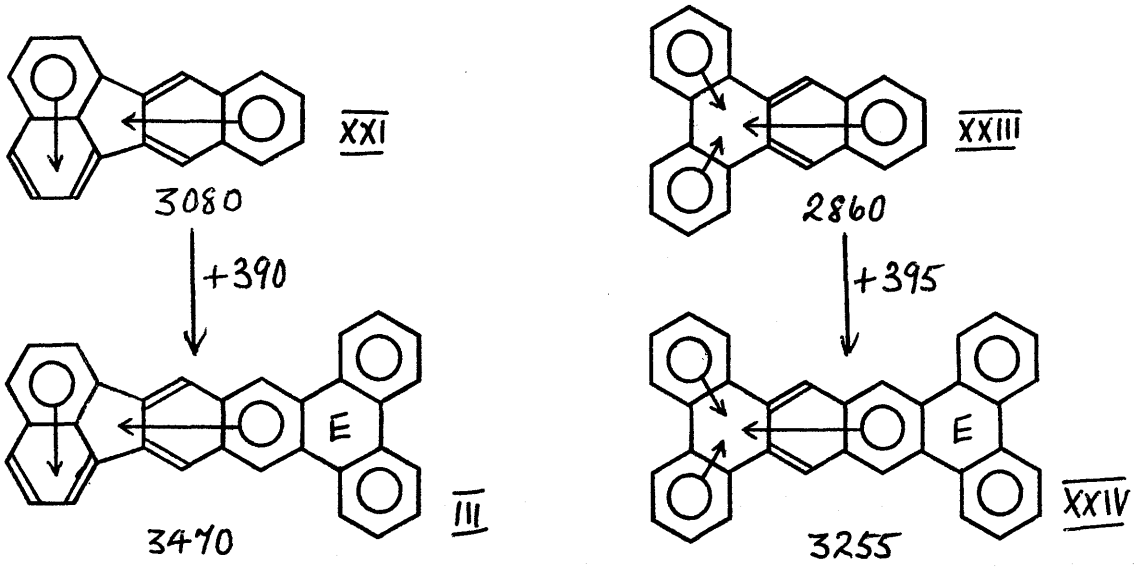


Figure 4. Absorption max. (A°) and log ε (in parentheses). 2.3, 6.7 - Di - (peri - naphthylene) - anthracene in benzene, p: 4730 (4.66), 4420 (4.46), 4160 (4.12), 4030 (4.00); β: 3540 (5.22), 3380 (4.96); in cyclohexane, β': 2700 (4.80), 2570 (4.98).

(XXIII) to 1.2, 3.4, 7.8, 9.10 - tetrabenzanthracene (XXIV).

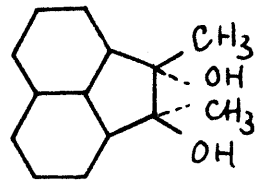


The shifts are + 390 and + 395 A° respectively, and in both cases an empty ring (E) is produced.

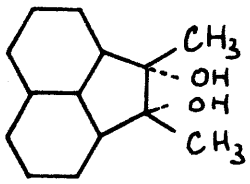
EXPERIMENTAL DISCUSSION: Acenaphthenequinone reacts with methyl magnesium iodide to give a mixture of the stereoisomeric cis (XXV) and trans 7.8 - dimethyl-acenaphthene - 7.8 - diols.[21] The separation of the isomers has been described by Criegee[22] and more recently by Tucker, and Tucker's method was employed. Campbell and Gow[23] have demonstrated that of the two forms only one form, the transform undergoes a Diels Alder reaction when dehydrated with boiling acetic anhydride in the presence of a dienophile. The preparation of 10. 11. 12. 13 - tetrahydrofluoranthene - 11.12 - dicarboxylic anhydride from trans diol (XXVI) and maleic anhydride and the dehydrogenation of (XXVII) to fluoranthene - 11.12 - dicarboxylic anhydride have been described by the above authors.

10. 11. 12. 13 - Fluoranthene - 11.12 - dicarboxylic anhydride (XXVII) was reduced with lithium aluminium hydride in boiling tetrahydrofuran to the diol (XXVIII). Treatment of this diol with phosphorus tribromide in boiling benzene gave a non halogen containing resinous product. Fluoranthene - 11.12 - dicarboxylic anhydride (XXIX) gave the diol (XXX) when reduced with lithium aluminium hydride. The hydroxyl groups were exchanged for bromine atoms with phosphorus tribromide in boiling benzene. Treatment of the dibromide (XXXI) with dry cuprous cyanide in boiling anhydrous xylene failed to yield the desired dinitrile (XXXII). However successful conversion to (XXXII) was achieved with ethanolic potassium cyanide.

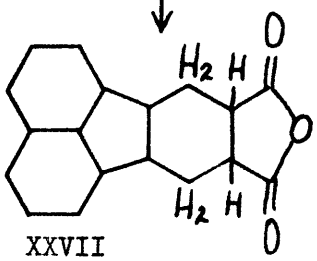
The base catalysed condensation of the dinitrile (XXXII) with acenaphthenequinone was accomplished in excellent yield by brief reflux of



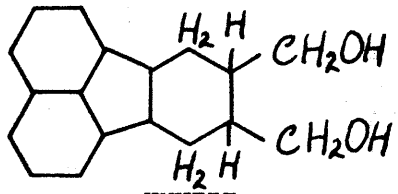
XXVI



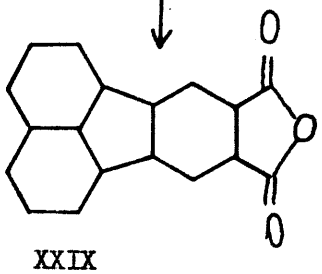
XXV



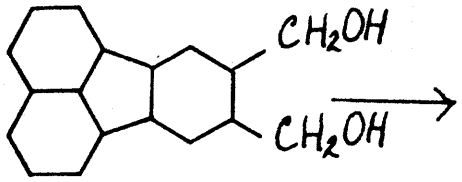
XXVII



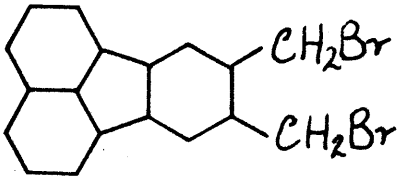
XXVIII



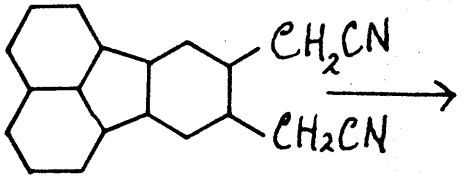
XXIX



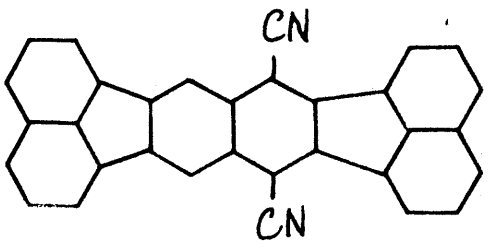
XXX



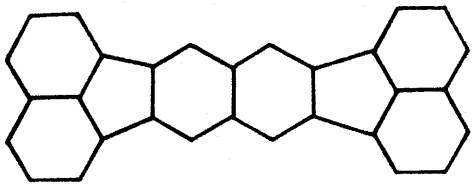
XXXI



XXXII



XXXIII

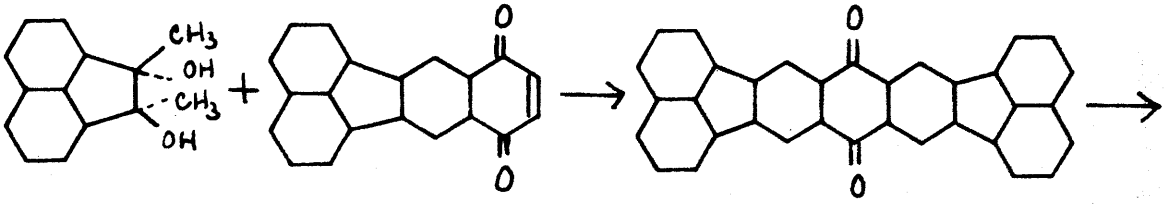


I

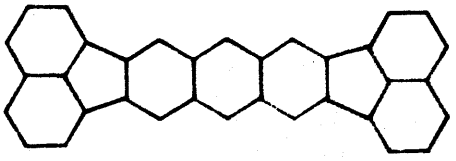
a solution of (XXXII) and acenaphthenequinone in pyridine, in the presence of piperidine as catalyst. The product of the condensation, the dinitrile (XXXIII), was high melting, sparingly soluble and extremely resistant to hydrolysis - recovered unchanged after refluxing for 24 hours with 20% potassium hydroxide in ethylene glycol. Hydrolysis and simultaneous decarboxylation to (I) occurred when the dinitrile (XXXIII) was heated at 400° with potassium hydroxide and soda lime. The hydrocarbon (I) was separated from the soda lime by sublimation in vacuo and was easily purified by chromatography.

The diene synthesis between trans 7.8 - dimethylacenaphthene - 7.8 - diol (XXVI) and 11.12 - benzofluoranthene - 1'.4' - quinone (XXXIV) leading to di - 2.3, 6.7 - (peri - naphthylene) - anthraquinone (XXXV) has been described by Campbell and Gow.[23] Reduction of the quinone to the hydrocarbon (II) was carried out by two methods. Zinc dust melt yielded the hydrocarbon (II) directly. Zinc dust pyridine acetic acid reduction furnished a yellow complex which was decomposed by heating it above its melting point in vacuo. The product of the decomposition was dehydrogenated to (II) by heating with copper powder at 320°.

11.12 - Benzofluoranthene - 1'.4' quinone (XXXIV) was submitted to a diene synthesis with octahydrodiphenyl. This resulted in the formation of the hydrogenated quinone (XXXVI). A zinc chloride, - sodium chloride melt followed by dehydrogenation with copper powder at 320° gave 1.2, 3.4 - dibenzo - 6.7 - (peri - naphthylene) - anthracene (III).



XXVI XXXIV XXXV



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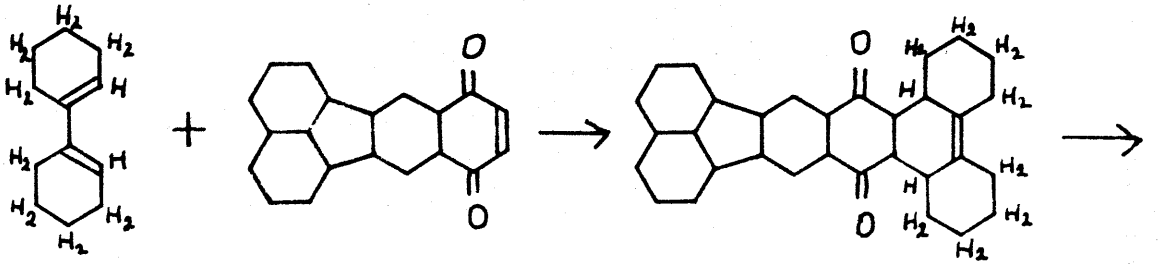
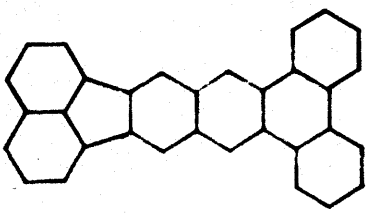


XXXIV XXXVI



III

EXPERIMENTAL.

10. 11. 12. 13 - Tetrahydro - 11.12 - bishydroxymethyl - fluoranthene (XXVIII).

To a stirred suspension of lithium aluminium hydride (0.8 g) in anhydrous tetrahydrofuran (50 ml) was added during the course of 20 minutes a solution of (XXVII) (5g) in tetrahydrofuran (75 ml). The reaction mixture after boiling for 2 hours, was cooled and decomposed with ice and dilute sulphuric acid. Extraction with ether and concentration of the dried (Na_2SO_4) ether extract gave the diol as an oil which solidified after trituration with 100 - 120° pet. ether. The diol (2.6 g) crystallized from xylene in yellow leaflets, m.p. 185 - 186°.

Found: C, 81.6; H, 6.8.

$C_{18}H_{18}O_2$ requires: C, 81.2; H, 6.8%.

11. 12 - Bishydroxymethylfluoranthene (XXX).

Compound (XXIX) (3.8g) in tetrahydrofuran (160 ml) was added during 15 minutes to a stirred suspension of lithium aluminium hydride (0.84g) in tetrahydrofuran (30 ml) and the mixture was heated under reflux for 2 hours. A deep red colour developed and persisted. The reaction mixture was decomposed by cautious addition of water and after acidification with dilute sulphuric acid the mixture was extracted with ether. Evaporation of the dried (Na_2SO_4) ether extract and crystallization from xylene furnished the diol (1.97g, 54%) as colourless needles, m.p. 180 - 181°.

Found: C, 82.1; H, 5.3.

$C_{18}H_{14}O_2$ requires: C, 82.4; H, 5.4%.

11.12 - Bisbromomethylfluoranthene (XXXI).

A suspension of (XXX) (1.97g) in dry benzene (250 ml) was treated with phosphorus tribromide (4.8g) and the mixture heated under reflux for 2 hours. The benzene solution was then washed with $NaHCO_3$ aqueous dried (Na_2SO_4) and evaporated. The residue of (XXXI) (1.9g, 65%) crystallized from benzene in small pale yellow prisms, m.p. 186 - 192°. Repeated crystallization from benzene gave the dibromide as thick pale yellow prisms, m.p. 197 - 198°.

Found: C, 56.3; H, 3.3; Br, 40.15.

$C_{18}H_{12}Br_2$ requires: C, 55.7; H, 3.1; Br, 41.2%.

11.12 - Biscyanomethylfluoranthene (XXXII).

Potassium cyanide (370 mg) was dissolved in as little water as possible and ethanol (80 ml) added. The mixture was heated to boiling and finely divided (XXXI) (1.0g) added in portions. After refluxing for 2 hours, the cooled reaction mixture was poured into water and the precipitated dicyanide (100 mg, 14%) crystallized from benzene in colourless needles or leaflets, m.p. 229 - 230°.

Found: N, 10.0.

$C_{20}H_{12}N_2$ requires: N, 10.0%.

Di - 2.3, 6.7 - (peri - naphthylene) - naphthalene - 1.4 dicyanide (XXXIII).

Compound (XXXII) (100 mg) and acenaphthenequinone (70 mg) were dissolved in pyridine (10 ml) and piperidine (0.5 ml) added. The solution was refluxed for 15 minutes during which time the yellow condensation product precipitated from solution. The precipitated yellow solid (120 mg, 79%) was filtered off and crystallized from nitrobenzene as yellow needles of (XXXIII), m.p. $> 500°$.

Found: C, 89.7; H, 3.4; N, 6.3.

$C_{32}H_{14}N_2$ requires: C, 90.1; H, 3.3; N, 6.6%.

Di - 2.3, 6.7 - (peri - naphthylene) - naphthalene (I).

An intimate mixture of the above dicyanide (100 mg) and soda lime

was made into a thick paste with saturated KOH aqueous and then heated for 5 minutes at 400° in an atmosphere of nitrogen. Traces of yellow sublimate were observed at this temperature and the major portion of the hydrocarbon was sublimed from the soda lime in vacuo. The yellow sublimate was dissolved in benzene and chromatographed on alumina. Development of the chromatogram gave a single yellow band which was eluted with benzene. Evaporation of the solvent and crystallization of the yellow solid thus obtained from xylene gave (I) (20 mg) as yellow needles or leaflets, m.p. 368 - 370°. The hydrocarbon shows a strong blue fluorescence in organic solvents and dissolves very slowly in concentrated sulphuric acid to give a green solution.

Found: C, 95.6; H, 4.55.

$C_{30}H_{16}$ requires: C, 95.7; H, 4.3%.

Decahydro - 1.2, 3.4 - dibenzo - 6.7 - (peri - naphthylene) - anthraquinone (XXXVI).

Octahydrodiphenyl (1.9g) and (XXXIV) (3.3g) were melted together and the resulting deep red viscous oil heated to boiling for a few seconds. The deep red glass which formed on cooling gave, after repeated crystallization from xylene, (XXXVI) (530 mg) as bright yellow needles, m.p. 300 - 301°. The quinone gives a violet vat with alkaline sodium dithionite and dissolves in concentrated sulphuric acid to give a dark green solution which changes to violet on standing.

Found: C, 86.7; H, 5.9.

$C_{32}H_{26}O_2$ requires: C, 86.8; H, 5.9%.

1.2, 3.4 - Dibenzo - 6.7 - (peri - naphthylene) - anthracene (III).

The above quinone (850 mg) and sodium chloride (850 mg) were ground together. Zinc chloride (4.25g) was added and the mixture melted, the temperature being raised to 320° for 4 minutes. The colour of the melt was red-brown. The zinc chloride was removed with dilute acetic acid, the residue washed with ammonia and water, dried and dehydrogenated with copper powder at 300° under carbon dioxide for 4 minutes. Sublimation in vacuo gave (III) (200 mg) as small yellow needles which crystallized from xylene in thin bright yellow needles, m.p. 344 - 346°.

Found: C, 95.2; H, 4.6.

$C_{32}H_{18}$ requires: C, 95.5; H, 4.5%.

The hydrocarbon exhibits a blue fluorescence in organic solvents and dissolves slowly in concentrated sulphuric acid to give a yellow - brown solution.

Di - 2.3, 6.7 - (peri - naphthylene) - anthracene (II).

Compound (XXXV) (1g) was ground together with zinc dust (1g) sodium chloride (1g) and moist zinc chloride (5g) added. The temperature was raised, with stirring to 320° for 4 minutes. After cooling the melt was digested with dilute acetic acid, the zinc dust dissolved in concentrated hydrochloric acid and the residue washed with ammonia and finally water. Sublimation in vacuo followed by crystallization of the brown-yellow sublimate from nitrobenzene gave (II) as golden yellow leaflets (100 mg),

m.p. 460°. The hydrocarbon shows a green fluorescence in organic solvents and dissolves very slowly in concentrated sulphuric acid to give a red-brown solution.

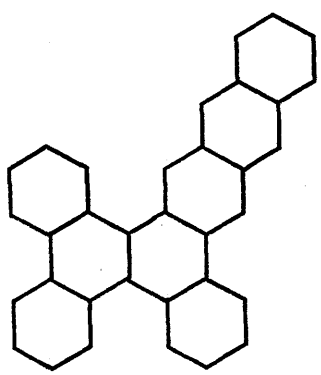
Found: C, 95.55; H, 4.3.

$C_{34}H_{18}$ requires: C, 95.7 ; H, 4.3%.

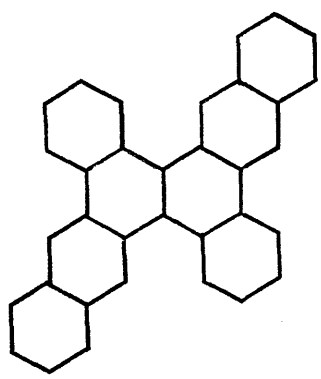
Compound (XXXV) (1g) and zinc dust (5g) were refluxed in pyridine (50 ml), contact with air being prevented by a mercury valve. Dilute acetic acid (95%, 14 ml) was added in portions at intervals of 1 hour over 6 hours. The solution, initially orange yellow in colour became red and this colour persisted. After 6 hours, the pyridine mother liquor was poured into dilute aqueous hydrochloric acid and the precipitated yellow solid filtered off and washed with ammonia and water. After drying the reduction product was heated together with copper powder at 320° under carbon dioxide for 5 minutes. The hydrocarbon (80 mg) was sublimed from the copper in vacuo and was identical to the sample obtained in the zinc dust melt, m.p. and mixed m.p. 460°.

C H A P T E R II.

1.2 - BENZOPHENANTHRENO - (9'.10' - 3.4) - TETRACENE and TETRAPHENO - (6'.5' - 5.6) - TETRAPHENE.



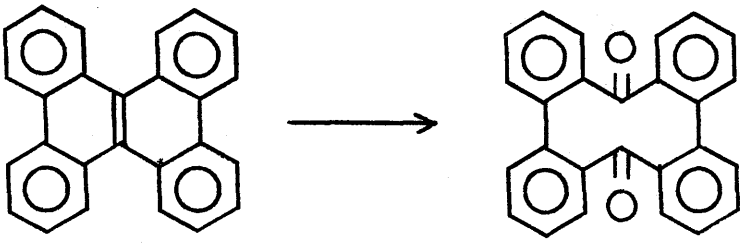
III



IV

INTRODUCTION: 1.2, 7.8 - Dibenzochrysene (I) is so far the only naphthalene derivative known in which a double bond between two rings cleaves on oxidation to give a diketone (II).[1] This indicates that contrary to naphthalene a double bond

is fixed between the two rings.

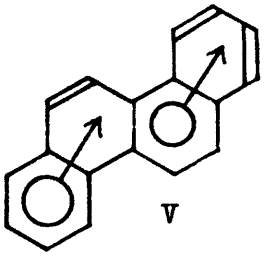


I II

The aim of the present work was to determine whether this bond fixation was preserved in higher benzologues of 1.2, 7.8 - dibenzochrysene. For this purpose two hydrocarbons, 1.2 - benzophenanthreno - (9'.10' - 3.4) - tetracene (III) and tetrapheno - (6'.5' - 5.6) - tetraphene (IV) were synthesised.

THEORETICAL DISCUSSION: In passing from chrysene (V) to 1.2, 7.8 - dibenzochrysene (I) (Figure I) a rather big red shift of both β and para-bands (+340 and + 320 Å respectively) is recorded. This shift could be composed of two components, namely the shift due to the fixation of the central double bond and the shift associated with the formation of the overcrowded positions (marked*).[2]

Much smaller red shifts (150 and 140 Å respectively) for the β - bands are observed in going from anthracenoanthracene (VI)[3] to tetrapheno-tetraphene (IV) (Figure II) and from naphthotetracene[4] (VII) to benzophen-anthrenotetracene (III) (Figure III). These shifts probably account for



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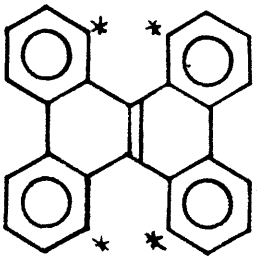
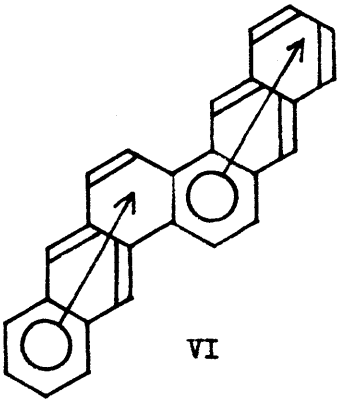


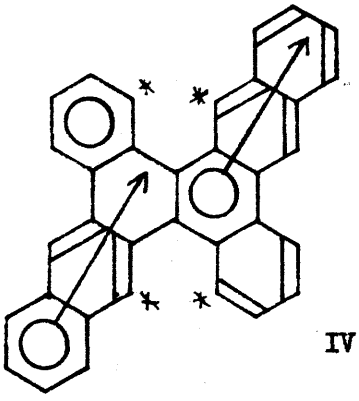
I

λ_β = 2670 (A) $\xrightarrow{+340}$ 3010 (A)

λ_p = 3190 (A) $\xrightarrow{+320}$ 3510 (A)



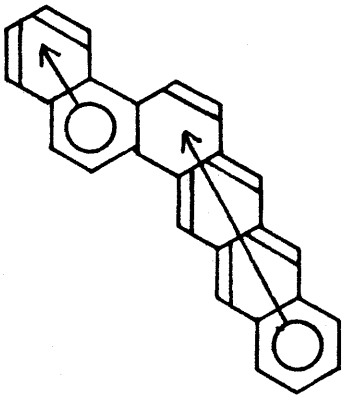
VI



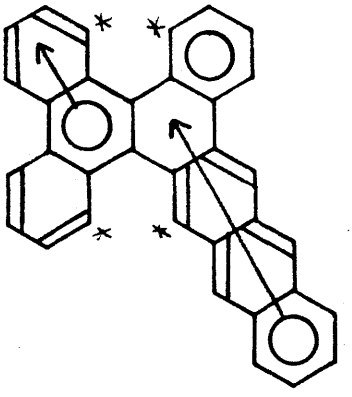
IV

λ_β = 3070 (B) $\xrightarrow{+150}$ 3220 (B)

λ_p = 4200 (B) $\xrightarrow{0}$ 4200 (B)



VII



III

λ_β = 3140 (B) $\xrightarrow{+140}$ 3280 (B)

λ_p = 4720 (B) $\xrightarrow{-60}$ 4660 (B)

Solvent A = alcohol, B = Benzene, C = Cyclohexane.

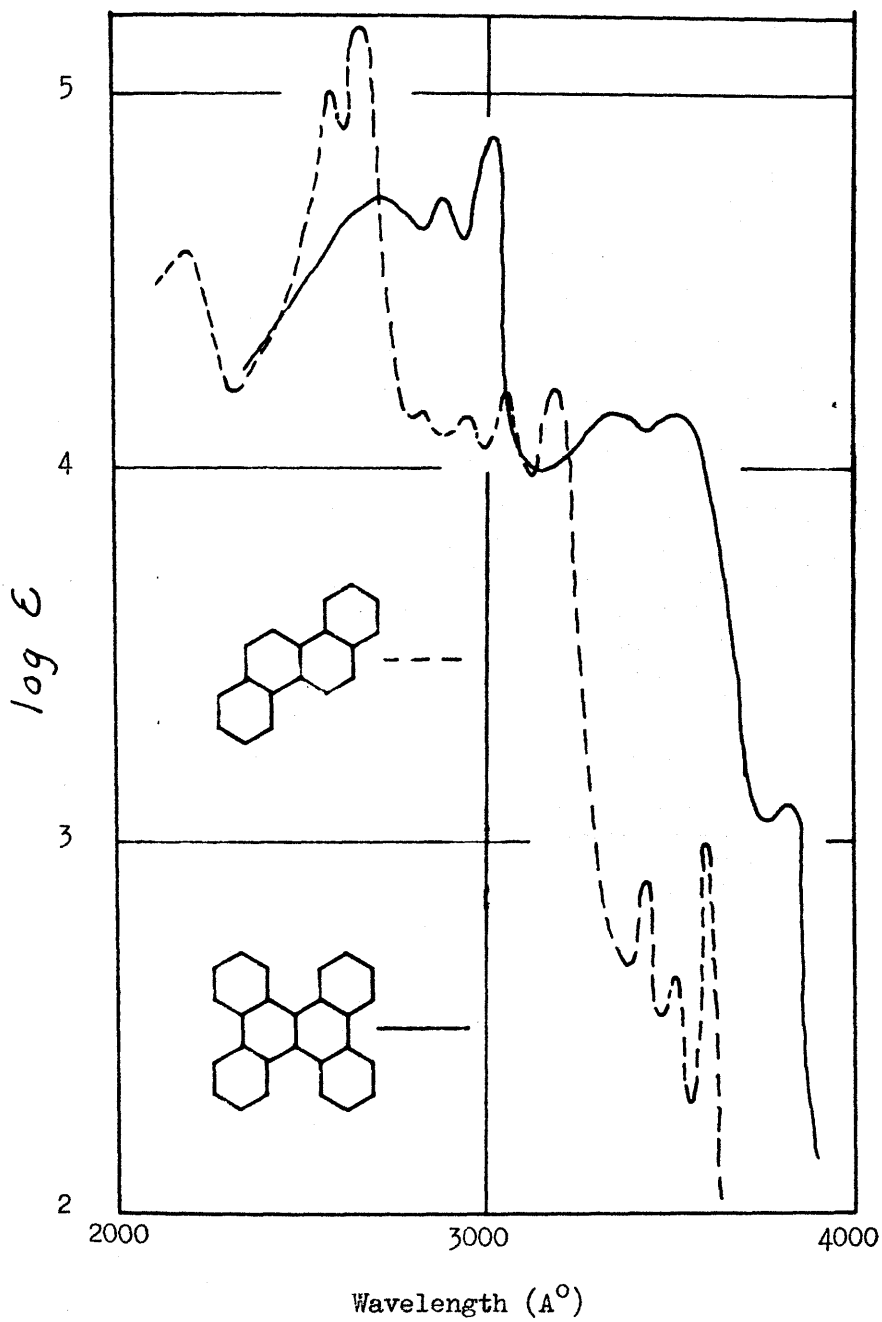


Figure 1. Absorption max. (Å) and log ε (in parenthesis). Chrysene in alcohol, α : 3600 (3.00), 3510 (2.62), 3435 (2.88); p: 3190 (4.19), 3060 (4.19), 2950 (4.13), 2830 (4.14); β : 2670 (5.20), 2590 (5.00); β': 2410 (4.36), 2200 (4.56). 1.2, 7.8 - Dibenzochrysene in alcohol, α : 3830 (3.10); p: 3510 (4.14), 3360 (4.16); β : 3010 (4.90), 2880 (4.72); β': 2700 (4.72).

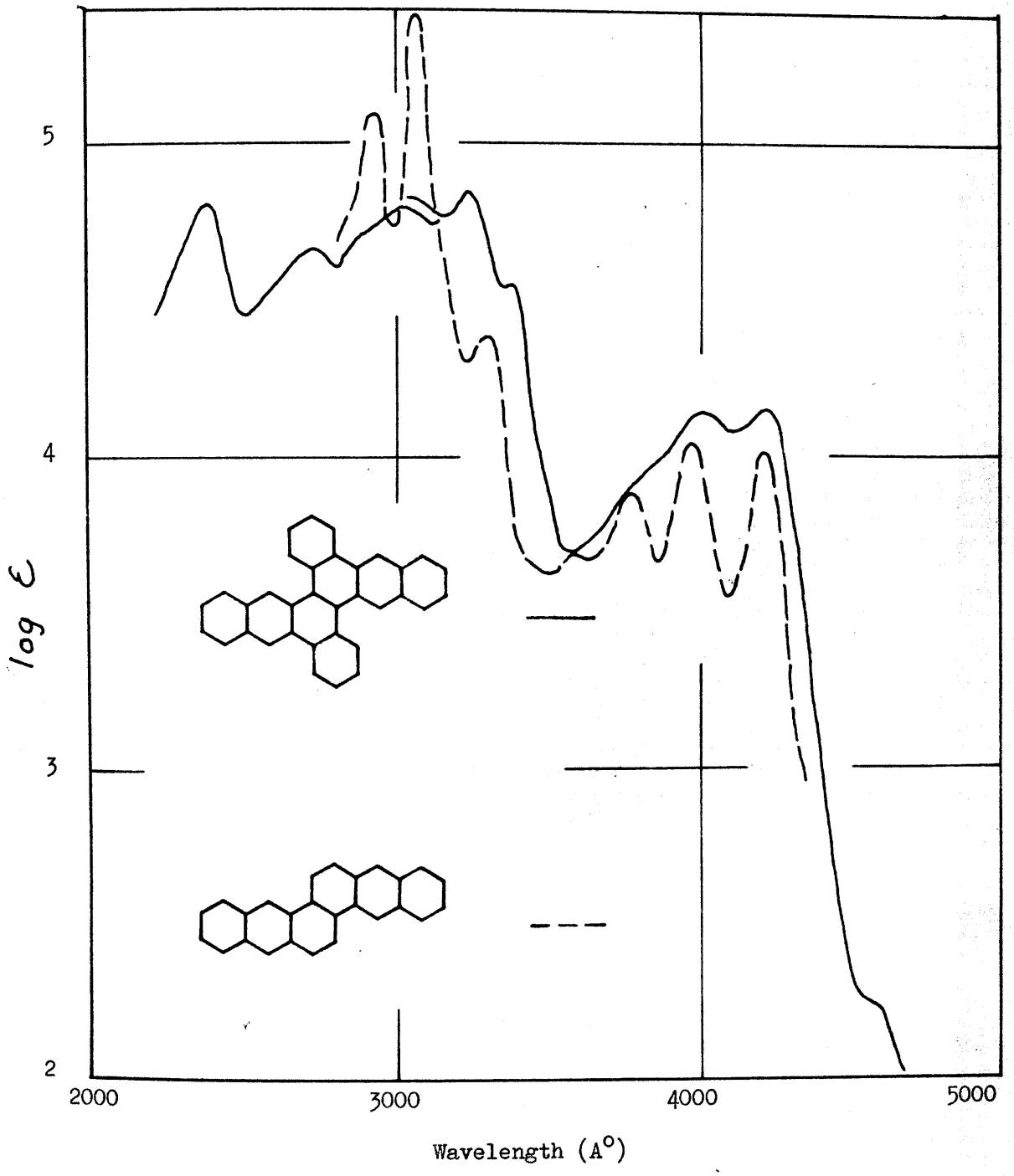


Figure 2. Absorption max. (A°) and log ε (in parentheses). Anthraceno - (2'.1' - 1.2) - anthracene in benzene, p: 4200 (4.03), 3960 (4.06), 3770 (3.90), 3580 (3.71); 3290 (4.40); β : 3070 (5.44), 2940 (5.11). Tetrapheno - (6'.5' - 5.6) - tetraphene in benzene, p: 4200 (4.14), 4000 (4.14); 3360 (4.54); β : 3220 (4.84), 3040 (4.81); in cyclohexane, 2720 (4.65); β' : 2400 (4.80).

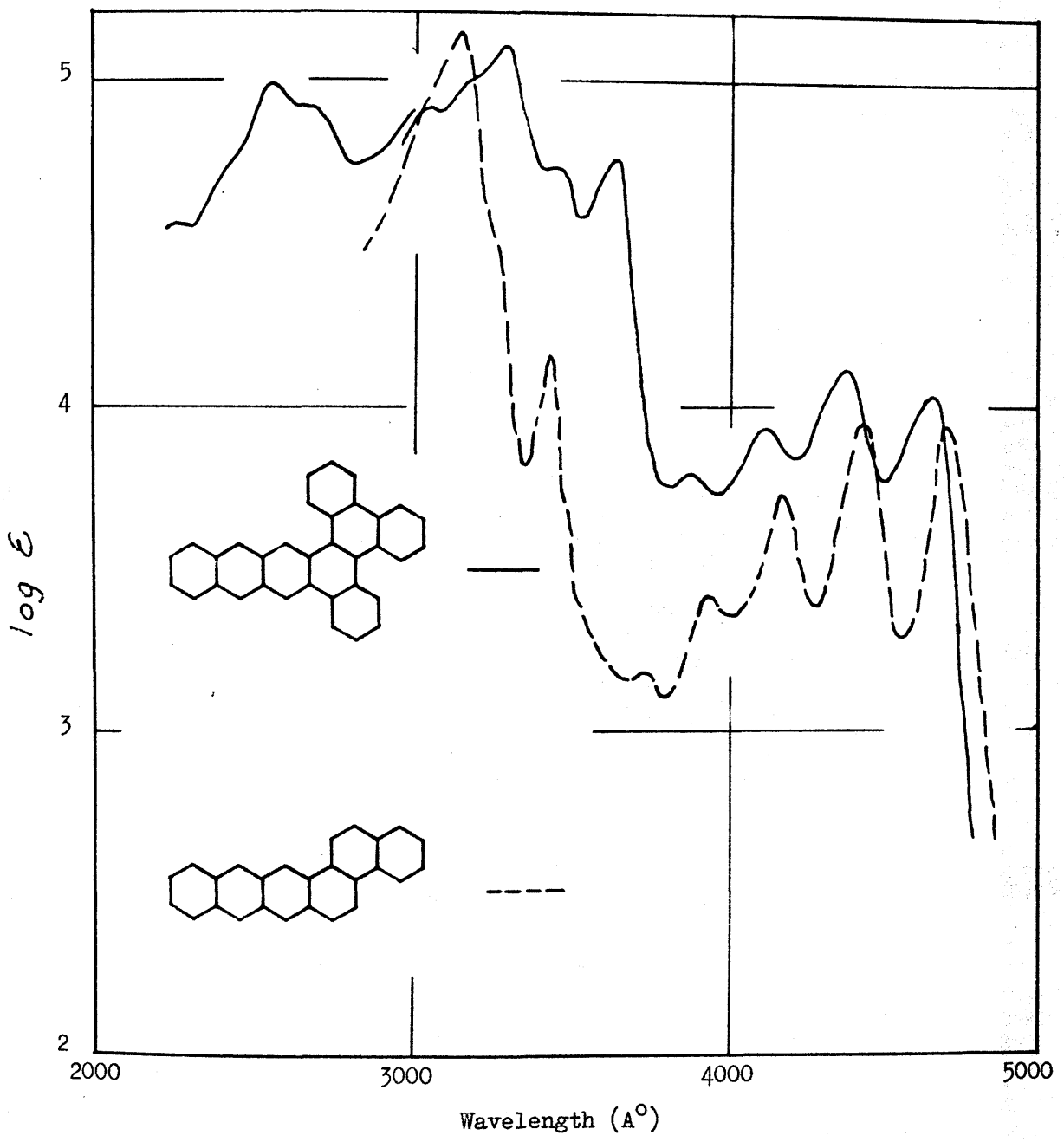
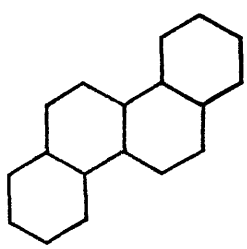
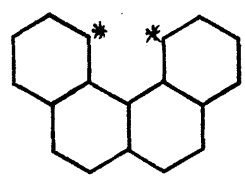


Figure 3. Absorption max. (A°) and log ε (in parentheses). Naphtho - (2'.1' - 1.2) - tetracene in benzene, p: 4720 (3.98), 4420 (3.98), 4160 (3.76), 3930 (3.46), 3760 (3.21); 3420 (4.20); β : 3140 (5.20) 3040 (4.98). 1.2 - Benzophenanthreno - (9'.10' - 3.4) - tetracene in benzene, p: 4660 (4.04), 4380 (4.12), 4120 (3.94), 3880 (3.78); 3620 (4.76), 3450 (4.74); β : 3280 (5.12), 3040 (4.92); in cyclohexane, 2680 (4.91), 2540 (5.00).

the formation of the overcrowded positions in (IV) and (III). The same difference of 140 A° of the β bands is recorded between chrysene and 3.4 - benzophenanthrene and is due to overcrowding.[5]





λ_{β} = 2670 $\xrightarrow{+140}$ 2810 A°

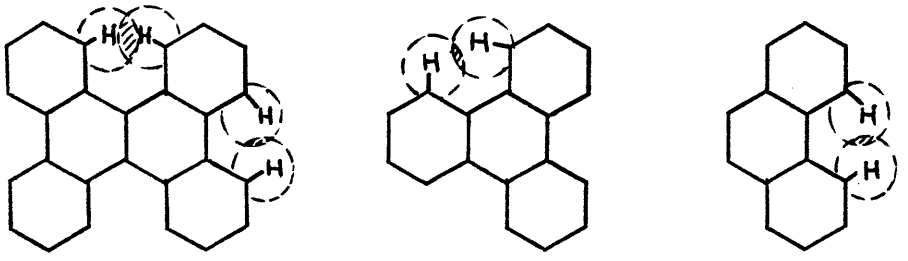
It must therefore be assumed that no fixation of a double bond has taken place in (IV) and (III). This view is supported by the fact that the β - bands of (VI) and (VII) and of (IV) and (III) show almost the same difference (70 and 80 A° respectively).

The above conclusion based on annellation effect is substantiated by chemical evidence. Cleavage of the central double bond in 1.2, 7.8 - dibenzochrysene was taken as an indication that this double bond was fixed. If bond fixation is preserved in tetraphenotetraphene (IV) and benzophenanthrenotetracene (III) then oxidation should cleave the central naphthalene nucleus in IV and (III). When (IV) was oxidized tetrapheno - (6'.5' - 5.6) - tetraphene - 7'.12'. 7.12 - diquinone was obtained. The central naphthalene nucleus has remained intact. Thus oxidation supports the view that there is no fixed double bond in tetraphenotetraphene (IV).

Oxidation of benzophenanthrenotetracene (III) gave 2.3, 4.5,

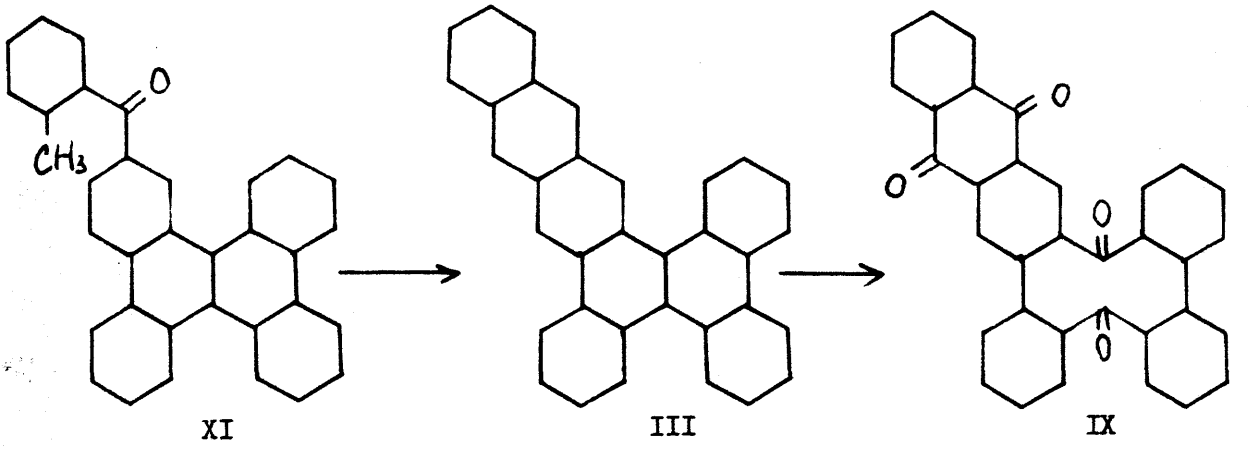
7.8 - tribenzanthraquinono - (2''''.3'''' - 9.10) - cyclodecane - 1.6 - dione (IX). The oxidation of (III) probably involves two stages, the first stage being the oxidation of the long acene branch giving the quinone (X). (X) contains the 1.2, 7.8 - dibenzochrysene skeleton which will oxidize during the second stage in the same way as 1.2, 7.8 - dibenzochrysene, that is the central double bond will cleave to give (IX). Thus the formation of (IX) does not prove bond fixation in (III).

EXPERIMENTAL DISCUSSION: No Friedel - Crafts reactions involving the 1.2, 7.8 - dibenzochrysene molecule have hitherto been described. There are four possible positions (positions 3, 4, 5 and 6) at which substitution can occur. The 3 and the 6 -positions are sterically overcrowded. A lack of reactivity has been observed at the 1-position of triphenylene and the 4-position of phenanthrene and has been attributed to steric overcrowding at these positions.



A similar lack of reactivity would be expected at the 3-position of 1.2, 7.8 - dibenzochrysene which has the same environment as the 1-position of triphenylene and the 4-position of phenanthrene. A lack of reactivity again due to overcrowding can also be predicted for the 6-position of 1.2, 7.8 - dibenzochrysene. This leaves the 4 and 5 -positions.

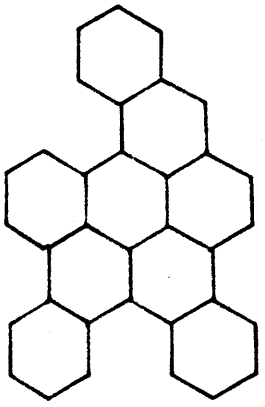
Condensation of 1.2, 7.8 - dibenzochrysene and one molecule of o - toluyl chloride in the presence of aluminium chloride gave a uniform ketone 4 or 5 - (o - toluyl) - 1.2, 7.8 - dibenzochrysene. This ketone was pyrolysed at 420-430^{o} under the protection of carbon dioxide. The pyrolysate was extracted with xylene and when the xylene extract was concentrated a red hydrocarbon crystallized from solution. It was purified



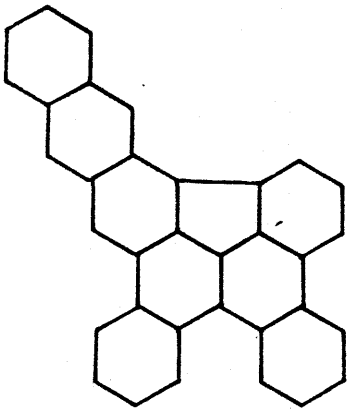
XI

III

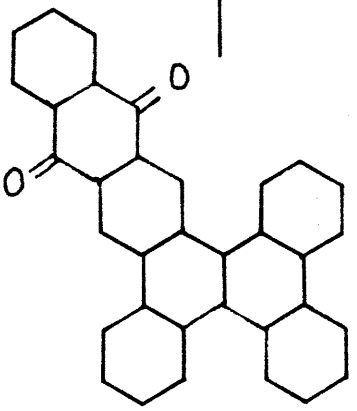
IX



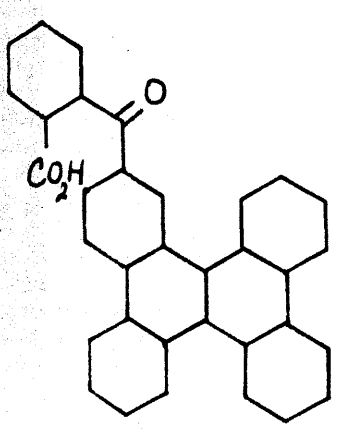
XIII



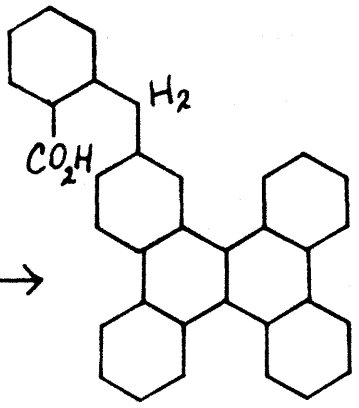
XII



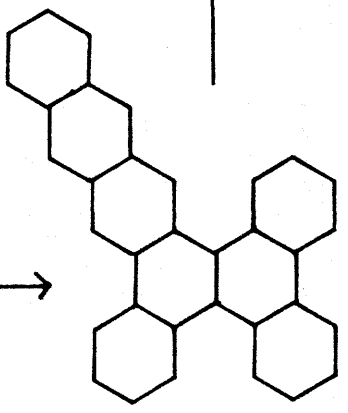
X



XIV



XV



III

by sublimation in vacuo and from a consideration of its analytical figures and spectrum (Figure IV) it is suggested that this hydrocarbon is 5.6 - benzo - naphtho (2''.3'' - 12.13) - 7.10 - (o - phenylene) - fluoranthene (XII). Chromatography of the xylene mother liquor resulted in the separation of two hydrocarbons, 1.2 - Benzophenanthreno - (9'.10' - 3.4) - tetracene (III) (Spectrum Figure III) the major product of the pyrolysis, and a second hydrocarbon which according to its analytical data and spectrum (Figure IV) is probably 2.3, 7.8 - dibenzo - 1.12 (o - phenylene) - perylene (XIII).

A normal Elbs cyclization of either 4 or 5 - (o - toluyl) - 1.2, 7.8 - dibenzochrysene would furnish 1.2 - benzophenanthreno - (9'.10' - 3.4) - tetracene (III). The formation of 2.3, 7.8 - dibenzo - 1.12 - (o - phenylene) - perylene (XIII) on the other hand, requires a rather unusual Elbs cyclization of 5 - (o - toluyl) - 1.2, 7.8 - dibenzochrysene at the 6-position and a subsequent dehydrogenation. Thus, while the formation of 2.3, 7.8 - dibenzo - 1.12 - (o - phenylene) - perylene (XIII) in the pyrolysis of o - toluyl 1.2, 7.8 - dibenzochrysene, suggests that Friedel - Crafts substitution of 1.2, 7.8 - dibenzochrysene occurs at the 5-position it is not possible to say with any degree of certainty that substitution actually occurs at this position. It must be remembered that in a pyrolysis like the one described above, 4 - (o - toluyl) - 1.2, 7.8 - dibenzochrysene could also give rise to 2.3, 7.8 - dibenzo - 1.12 - (o - phenylene) - perylene if the o - toluyl group first migrated to position 5.

1.2 Benzophenanthreno - (9'.10' - 3.4) - tetracene (III) was

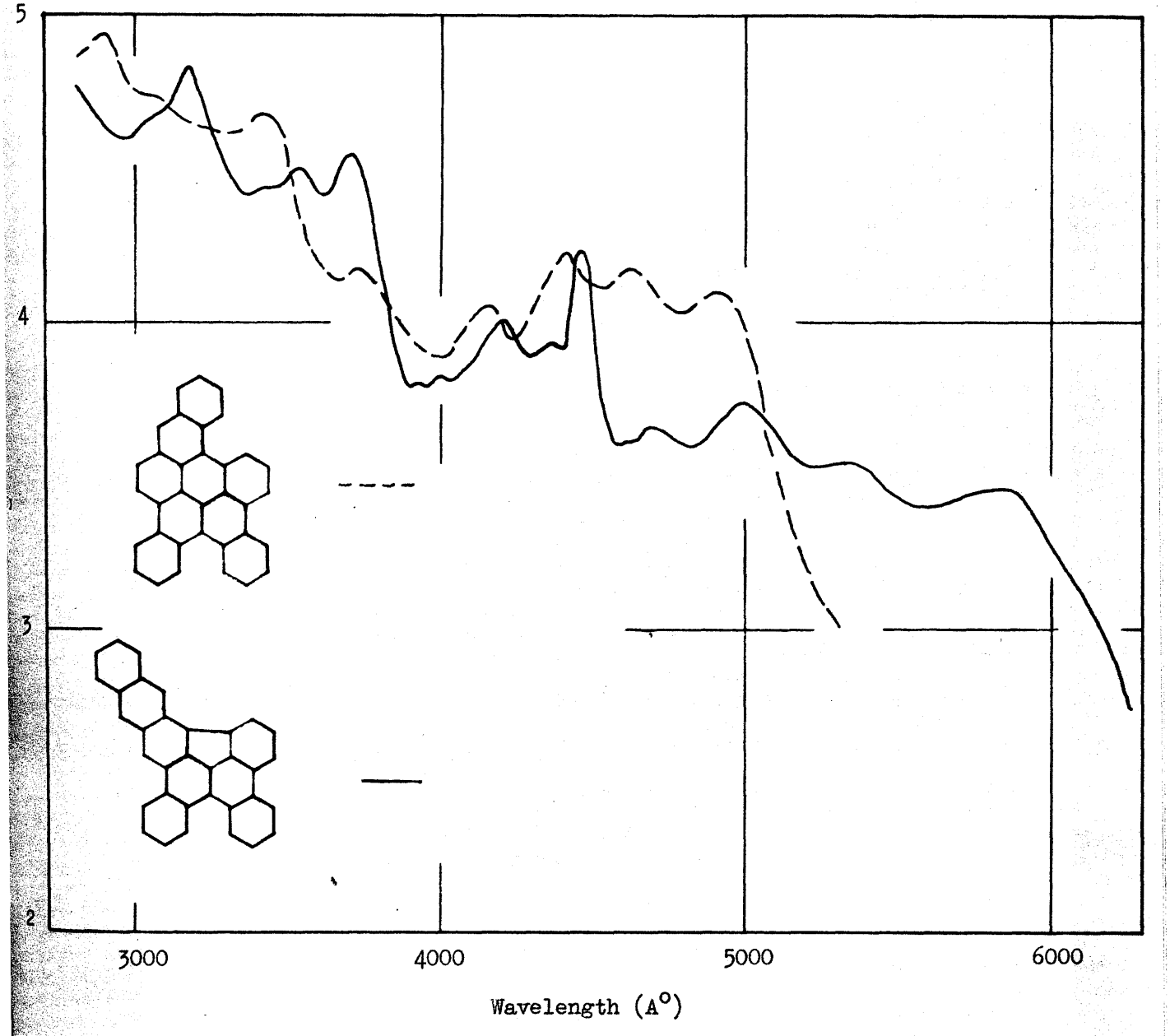


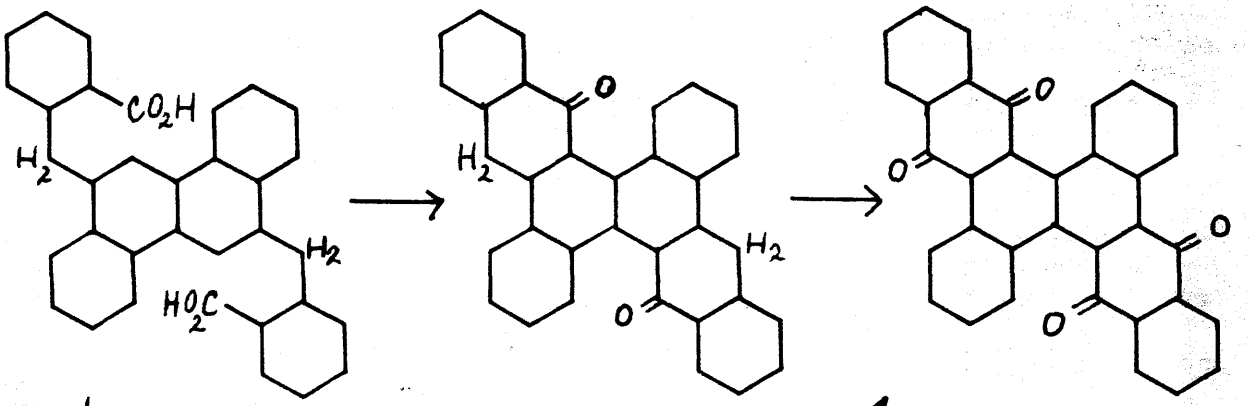
Figure 4. Absorption max. (A°) and log $\mathcal{E}$ (in parentheses). 2.3, 7.8 - Dibenzo - 1.12 - (o - phenylene) and perylene in benzene, 4900 (4.10), 4620 (4.18), 4410 (4.24), 4160 (4.06), 3720 (4.18); 3400 (4.69); 2890 (4.94). 5.6 - Benzo - 7.10 - (o - phenylene) - naphtho - (2'''.3''' - 2.3) - fluoranthene in benzene, 5840 (3.46), 5240 (3.57), 4980 (3.74), 4680 (3.66), 4460 (4.24), 4360 (3.94), 4200 (4.02), 4000 (3.84), 3940 (3.82), 3610 (4.56), 3540 (4.50), 3180 (4.84).

also synthesized from 1.2, 7.8 - dibenzochrysene, phthalic anhydride and aluminium chloride. The Friedel - Crafts reaction gave 5 - (o - carboxybenzoyl) - 1.2, 7.8 - dibenzochrysene (XIV). This keto-acid could not be cyclized with benzoyl chloride and sulphuric acid and was reduced to 5 - (o - carboxybenzyl) - 1.2, 7.8 - dibenzochrysene (XV) with zinc and acetic acid. A zinc dust melt on the above acid gave 1.2 - benzophenanthreno - (9'.10' - 3.4) - tetracene (III).

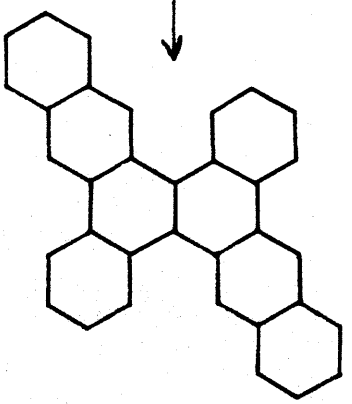
When 1.2 - benzophenanthreno - (9'.10' - 3.4) - tetracene was oxidized with chromic anhydride in glacial acetic acid 2.3, 4.5, 7.8 - tribenzanthraquinono - (2''''.3'''' - 9.10) - cyclodecane - 1.6 - dione (IX) was obtained.

2.8 - Di - (o - carboxybenzyl) - chrysene (XVI)[6] which can be obtained from chrysene in four stages was cyclized, with concentrated sulphuric acid to the compound (XVII). Compound (XVII) was rather sensitive to aerial oxidation and was immediately dissolved in pyridine and reduced with zinc dust and acetic acid. During the course of the reduction a small amount of tetrapheno - (6'.5' - 5.6) - tetraphene (IV) crystallized from solution. However the major product of the reduction was a yellow complex of the reduced quinone with pyridine and zinc acetate. This complex decomposed when heated above its melting point in vacuo to give tetrapheno - (6'.5' - 5.6) - tetraphene (IV) which was purified by chromatography.

Oxidation of tetrapheno - (6'.5' - 5.6) - tetraphene (IV) with chromic anhydride in glacial acetic acid furnished a diquinone which was given the structure (VIII). That the oxygen atoms had been assigned to



XVI XVII VIII



IV

the correct positions was confirmed when the same diquinone (VIII) was obtained on oxidizing compound (XVII) with chromic anhydride.

Since this work has been completed Martin et al.[7] have published a paper in which tetrapheno - (6'.5' - 5.6) - tetraphene (IV) is mentioned. No experimental details are given. However it is stated that the synthesis of (IV) furnishes an isomeric hydrocarbon, tetrapheno - (5'.6' - 5.6) - tetraphene and this synthesis is obviously different from the synthesis described above. The melting point of Martin's tetraphenotetraphene 332 - 335° indicates that this and the above tetraphenotetraphene (IV) are identical. Furthermore from a consideration of the N.M.R. spectra of mono acetyl 1.2, 7.8 - dibenzochrysene and the mono ethyl derivative derived from the mono acetyl derivative in conjunction with degradative evidence, Martin et al. have shown that monosubstitution of 1.2, 7.8 - dibenzochrysene gives the 4-monosubstitution product.

EXPERIMENTAL

5 - (o - Toluyl) - 1.2, 7.8 - dibenzochrysene (XI).

Finely ground aluminium chloride (9.2g) was added to a mixture of powdered 1.2, 7.8 - dibenzochrysene (I) (10g) and o - toluyl chloride (4.75g) in benzene (40 ml), the colour immediately becoming dark red and hydrogen chloride being evolved. The mixture was permitted to stand at room temperature for 8 minutes, when the double compound was decomposed with dilute hydrochloric acid and the benzene removed by steam distillation. The yellow brown residue was powdered and extracted with dilute aqueous ammonia leaving the crude ketone (12g). A portion of the ketone was crystallized from acetic acid. A second crystallization from benzene gave (XI) as white prisms, m.p. 214 - 215°. The ketone dissolves in concentrated sulphuric acid to give a violet changing to red solution.

Found: C, 91.35; H, 4.9.

$C_{34}H_{22}O$ requires: C, 91.4; H, 5.0%.

Pyrolysis of 5 - (o - toluyl) - 1.2, 7.8 - dibenzochrysene (XI).

Crude 5 - (o - toluyl) - 1.2, 7.8 - dibenzochrysene (15g) was dissolved in xylene and the xylene solution filtered. The xylene was removed by distillation and the residue was pyrolysed at 420 - 430° for 10 minutes under carbon dioxide. The pyrolysate (10g) was dissolved in xylene and the xylene solution concentrated to small volume. On standing a violet red compound A (440 mg) crystallized from solution. The xylene mother liquor was chromatographed on alumina grade I. Two fractions were eluted with xylene. Concentration of the first gave thick orange-yellow needles of B (1.5g), m.p. 240 - 244° and concentration of the second fraction gave fibrous orange-yellow needles of C (100 mg), m.p. 280 - 282°. Eluting with xylene - ether mixture gave a further (20 mg) of A.

A crystallized from a large volume of xylene in small red sublimable needles of 5.6 - benzo - naphtho - (2''.3'' - 12.13) - 7.10 - (o - phenylene) - fluoranthene (XII), m.p. 348 - 350°. (XII) dissolves in concentrated sulphuric acid to give a violet solution which changes to brown on standing.

Found: C, 95.85; H, 4.5.

$C_{34}H_{18}$ requires: C, 95.7 ; H, 4.3%.

Repeated crystallization of B gave orange-yellow needles of 1.2 - benzophenanthreno - (9'.10' - 3.4) - tetracene (III), m.p. 247 - 248°. In concentrated sulphuric acid the surface of the crystals becomes

very dark and (III) dissolves to give a green-brown solution.

Found: C, 95.4; H, 4.6.

$C_{34}H_{20}$ requires: C, 95.3; H, 4.7%.

Crystallization of C from xylene gave 2.3, 7.8 - dibenzo - 1.12 - (o - phenylene) - perylene (XIII) as fibrous orange-yellow needles, m.p. 282°. (XIII) dissolves in concentrated sulphuric acid to give an emerald green solution which becomes intense dark green on standing.

Found: C, 95.8; H, 4.2.

$C_{34}H_{18}$ requires: C, 95.7; H, 4.3%.

5 - (o - Carboxybenzoyl) - 1.2, 7.8 - dibenzochrysene (XIV).

An intimate mixture of finely divided phthalic anhydride (2.70g) and aluminium chloride (7.4g) was added in portions to a suspension of 1.2, 7.8 - dibenzochrysene (6g) in benzene (40 ml). A dark red complex formed immediately and after the evolution of hydrogen chloride had ceased (12 min.) the double compound was decomposed with dilute hydrochloric acid, the benzene steam distilled off and the pale yellow residue extracted with dilute aqueous ammonia. Acidification of the filtered alkali extract furnished 5 - (o - carboxybenzoyl) - 1.2, 7.8 - dibenzochrysene (6.0g) which crystallized from xylene or anisole in pale yellow prisms, m.p. 178 - 180°.

Found: C, 85.2; H, 4.6.

$C_{34}H_{20}O_3$ requires: C, 85.7; H, 4.2%.

5 - (o - Carboxybenzyl) - 1.2, 7.8 - dibenzochrysene (XV).

The above keto-acid (13g) was dissolved in acetic acid (260 ml) and zinc dust (39g) added in portions to the boiling solution. The yellow colour of the solution was discharged rapidly and after refluxing for 12 hours the colourless acetic acid mother liquor was poured into water and the precipitated white solid (8.5g) filtered off, boiled with conc. hydrochloric acid, washed with water and extracted with dilute aqueous sodium carbonate. The carbonate insoluble material (5.0g) (probably phthalide) was filtered off and acidification of the milky white carbonate extract gave 5 - (o - carboxbenzyl) - 1.2, 7.8 - dibenzochrysene (2.4g). The acid could not be obtained in a pure state and was used in the crude form for the next reaction.

1.2 - Benzophenanthreno - (9'.10' - 3.4) - tetracene (III).

5 - (o - Carboxybenzyl) - 1.2, 7.8 - dibenzochrysene (XV) (500 mg) was ground together with sodium chloride (500 mg) and zinc dust (500 mg). Zinc chloride (2.5g) was added and the mixture melted, the temperature being raised to 320 - 330° for 4 minutes. After the usual decomposition with dilute acetic acid the residue was extracted with xylene and chromatographed over alumina. Concentration of the orange-yellow eluate gave (III) (40 mg) as needles, m.p. and mixed m.p. with a sample from the pyrolysis of 5 - (o - toluyl) - 1.2, 7.8 - dibenzochrysene, 247 - 248°.

2.3, 4.5, 7.8 - Tribenzanthraquinono - (2''''.3'''' - 9.10) - cyclodecane - 1.6 - dione (X).

Finely powdered (III) (250 mg) was suspended in glacial acetic acid (15 ml). Chromium trioxide (260 mg) in water (2 ml) was added and the mixture refluxed for 3 hours. The cold mixture was poured into water and the precipitated oxidation product (290 mg) was filtered off. Crystallization from xylene furnished (X) as small white leaflets, m.p. 300°. (X) dissolves in concentrated sulphuric acid, orange changing to yellow on standing.

Found: C, 83.5; H, 3.9.

$C_{34}H_{18}O_4$ requires: C, 83.3; H, 3.7%.

Tetrapheno - (6'.5' - 5.6) - tetraphene (IV).

2.8 - Di - (o - Carboxybenzyl) - chrysene (XVI) (5g) was dissolved in concentrated sulphuric acid (70 ml). The acid, insoluble in the first instant dissolves to give a red-brown changing to red solution. The mixture was allowed to stand at room temperature for 10 minutes when the red solution was poured onto ice and the precipitated bright yellow cyclization product filtered off and washed with water. The moist diketone (XVII) was dissolved in hot pyridine (100 ml), zinc dust (10g) and glacial acetic acid (10 ml) were added and the mixture heated under reflux for $3\frac{1}{2}$ hours. The solution, initially orange-yellow became yellow and after about 1 hour small prisms of hydrocarbon crystallized from solution. Two additional portions of acetic acid (10 ml and 5 ml) were added at intervals of 1 hour. The cold pyridine mother liquor was filtered

from excess zinc and crystallized hydrocarbon into dilute hydrochloric acid and the precipitated yellow solid filtered off and washed with ammonia and water. Excess zinc was destroyed with concentrated hydrochloric acid and the crystallized hydrocarbon was combined with the yellow complex. The complex was decomposed by sublimation in vacuo. The sublimate, a yellow oil was dissolved in xylene and chromatographed on alumina grade I. Development of the chromatogram with xylene gave a single yellow band which was eluted with xylene. Concentration of the yellow eluate gave tetrapheno - (6'.5' - 5.6) - tetraphene (IV) (420 mg) as clusters of small bright yellow needles, m.p. 320 - 326°. (IV) was dissolved in xylene and rechromatographed on alumina. The chromatogram was eluted with hot xylene and concentration of the first fractions gave pure (IV) as yellow needles, m.p. 339 - 340°. The hydrocarbon dissolves slowly in concentrated sulphuric acid to give a yellow solution.

Found: C, 95.2; H, 4.7.

$C_{34}H_{20}$ requires: C, 95.3; H, 4.7%.

Tetrapheno - (6'.5' - 5.6) - tetraphene - 7'.12', 7.12 - diquinone (VIII).

Tetrapheno - (6'.5' - 5.6) - tetraphene (IV) (100 mg) was suspended in glacial acetic acid (10 ml) and chromium trioxide (150 mg) in water (1 ml) was added. The mixture was refluxed for 2 hours and the brown-red oxidation product which had precipitated from solution was filtered off and extracted with dilute aqueous ammonia leaving a brown-red powder (80 mg). Repeated crystallization from nitrobenzene gave

the diquinone (VIII) as violet-red needles, m.p. 374° dec. (VIII) dissolves slowly in concentrated sulphuric acid to give a blue-green solution which changes to violet on standing.

Found: C, 83.4; H, 3.2.

$C_{34}H_{16}O_4$ requires: C, 83.6; H, 3.3%.

The diquinone (VIII) from the diketone (XVII)

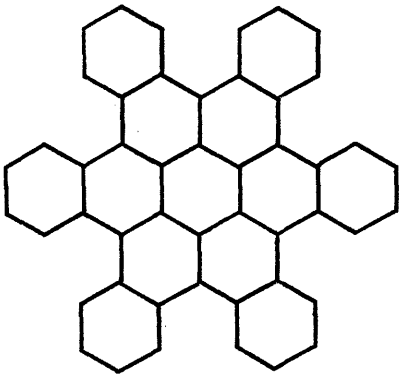
Moist diketone (XVII) from 2.8 - di - (o - carboxybenzyl) - chrysene (1g) and concentrated sulphuric acid (14 ml) was dissolved in glacial acetic acid (30 ml). Chromium trioxide (800 mg) in water (2 ml) was added and the mixture refluxed for 15 minutes. The precipitated brown-red solid (230 mg) was filtered off, extracted with hot dilute aqueous ammonia and crystallized from nitrobenzene. The diquinone crystallized as violet-red needles, m.p. and mixed m.p. with a sample obtained by direct oxidation of (IV) 374° dec.

Found: C, 83.5; H, 3.4.

$C_{34}H_{18}O_4$ requires: C, 83.6; H, 3.3%.

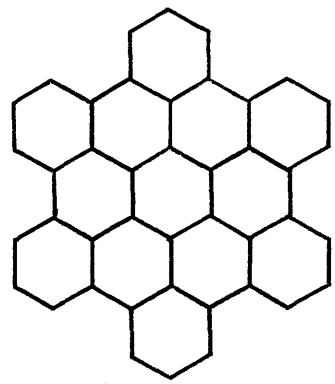
C H A P T E R III.

1.2, 3.4, 5.6, 7.8, 9.10, 11.12 - HEXABENZOCORONENE.



I.

INTRODUCTION: 1.2, 3.4, 5.6, 7.8, 9.10, 11.12 - Hexabenzocoronene (I) was synthesised for comparison with the fully benzenoid 1.12, 2.3, 4.5, 6.7, 8.9, 10.11 - hexabenzocoronene (II).[1]



II

THEORETICAL DISCUSSION: The absorption spectra of 1.2, 3.4, 5.6, 7.8, 9.10, 11.12 - hexabenzocoronene (I) and 1.12, 2.3, 4.5, 6.7, 8.9, 10.11 - hexabenzocoronene (II) are shown in (Figure I) and the similarity between them is immediately apparent.

Formula (Ia) shows that there are twelve overcrowded positions in hexabenzocoronene caused by the twelve hydrogen atoms (marked * in Ia). Obviously hexabenzocoronene cannot have a coplanar molecular structure but must assume a non-planar form in order to accommodate these hydrogen atoms. Many hydrocarbons exhibit intra-molecular overcrowding. Examples are diphenyl, triphenylene, 3.4 - benzophenanthrene[2] and hexahelicene[3] (III). Overcrowding is so extreme in hexahelicene (III) that this hydrocarbon exists in two optically active forms.[3]

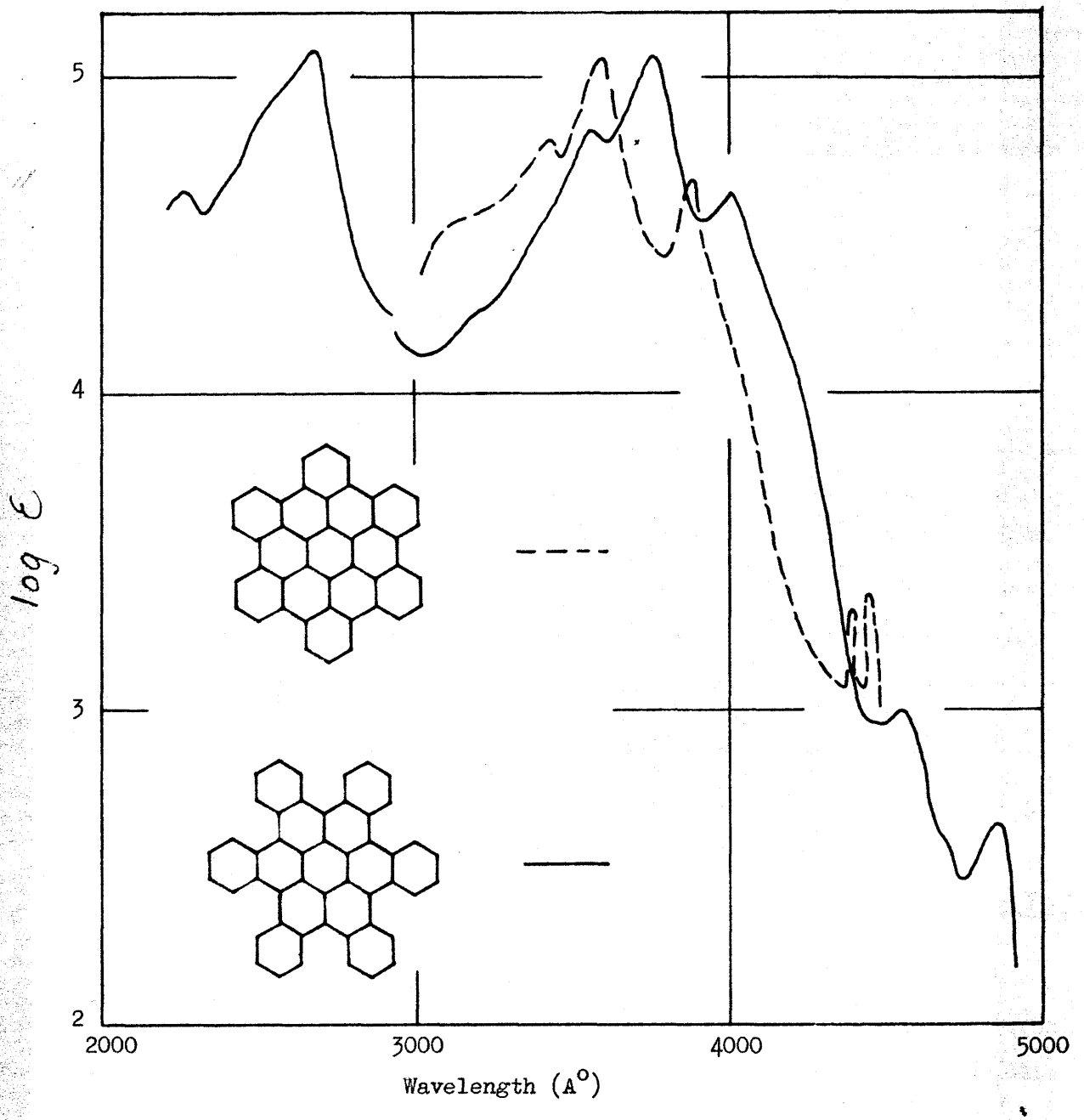
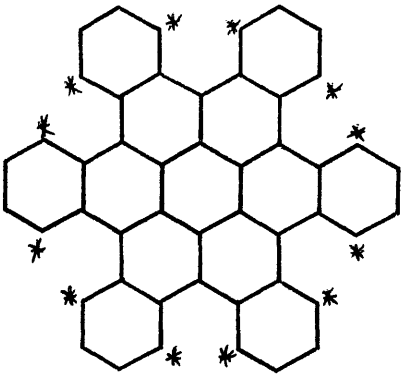
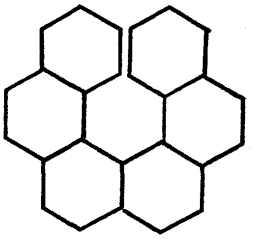


Figure 1. Absorption max. (A°) and log ε (in parentheses). 1.2, 3.4, 5.6, 7.8, 9.10, 11.12 - Hexabenzocoronene in benzene, α : 4860 (2.64), 4560 (3.01); p: 4020 (4.63); β : 3760 (5.07), 3570 (4.83); β' : 2680 (5.08), 2260 (4.64). 1.12, 2.3, 4.5, 6.7, 8.9, 10.11 - Hexabenzocoronene in 1.2.4 - trichlorobenzene. Owing to the low solubility the absolute intensities are uncertain log (ε + x), p: 3875 (4.68); β : 3600 (5.06), 3425 (4.80); α - bands were observed visually with a 100 cm. cell: 4440, 4380 (very sharp).



Ia



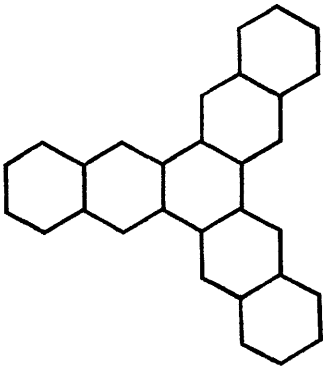
III

Overcrowded molecules have in general rather low melting points and have a greater solubility than would be expected from a consideration of their molecular weights. This latter characteristic manifests itself in 1.2, 3.4, 5.6, 7.8, 9.10, 11.12 - hexabenzocoronene (I) which has a molecular weight of 600 yet crystallizes from xylene or ψ- cumene. In striking contrast is the solubility of the planar hexabenzocoronene (II), molecular weight 522, which is insoluble in all conventional solvents and requires boiling pyrene to dissolve it.

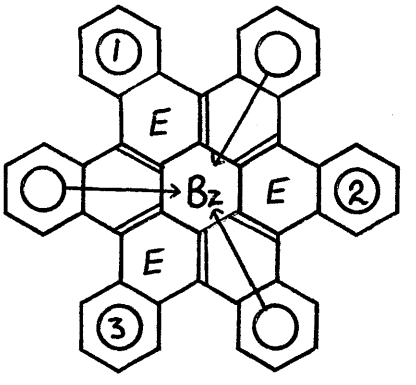
The ultra-violet spectra of sterically overcrowded molecules are affected in a characteristic way. Overcrowding brings about a broadening of the bands and the bands tend to be more shifted towards the red than would be expected from the predictions of the annellation principle.[4] Furthermore overcrowding has an influence on the $\lambda_\alpha : \lambda_\beta$ ratio. In planar molecules the $\lambda_\alpha : \lambda_\beta$ ratio is usually 1:1.35. In sterically overcrowded hydrocarbons this ratio decreases and typical values are: 1:1.24 in 1.2 - benzoperylene and 1:1.29 in 1.2, 5.6, 7.8, 11.12 - tetrabenzocoronene.[6]

The ratio for 1.2, 3.4, 5.6, 7.8, 9.10, 11.12 - hexabenzocoronene is 1:1.29.

1.2, 3.4, 5.6, 7.8, 9.10, 11.12 - Hexabenzocoronene can be derived from 2.3 - trinaphthylene (naphtho - [2'.3' - 6.7] - pentaphene) (IV)[7] by connecting the three o - phenylene groups 1, 2 and 3 in formula (Ib.).



IV

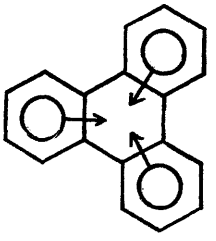


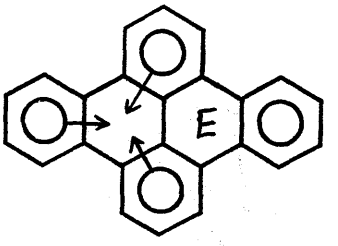
Ib.

λ_{β} = 3120 $\xrightarrow{+640}$ 3760 A°

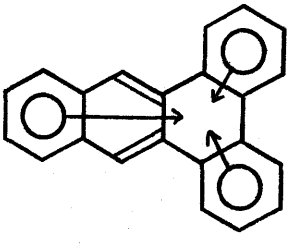
Two very different shifts are associated with o - phenylenation. The shift may be small and due entirely to the formation of the single bonds or in a so-called "benzenogenic annellation" the shift is large and is due to two components, the shift due to the formation of the single bonds and the shift associated with the formation of an induced benzenoid ring. Before discussing the tri - o - phenylenation of 2.3 - trinaphthylene, to give some idea of the values associated with the two different types of o - phenylenation, a variety of examples of both types are discussed below.

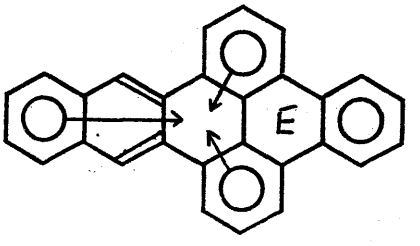
o - Phenylenation of 1.2, 3.4 - dibenzacenes gives the corresponding benzacenepyrenes. The shifts observed in passing from triphenylene, 1.2, 3.4 - dibenzanthracene[8] and 1.2, 3.4 - dibenzotetracene[9] to dibenzopyrene, benzonaphthopyrenene and benzanthracenopyrene[10] are 280, 260 and 300 A° respectively.



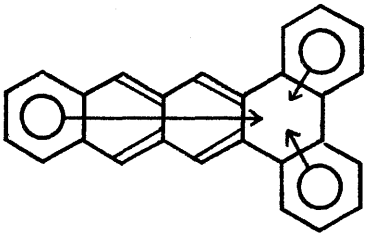


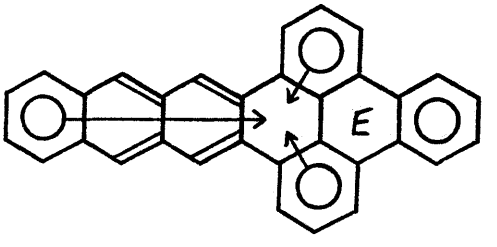
λ_β = 2570 $\xrightarrow{+280}$ 2850 Å





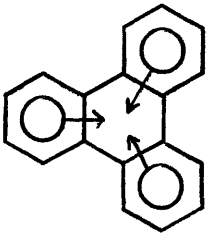
λ_β = 2900 $\xrightarrow{+260}$ 3160 A°

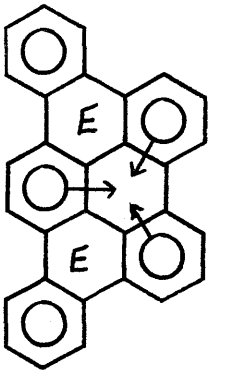




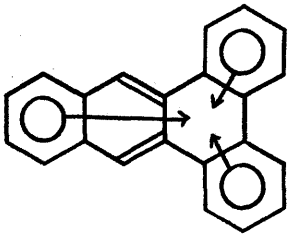
λ_β = 3180 $\xrightarrow{+300}$ 3480 A°

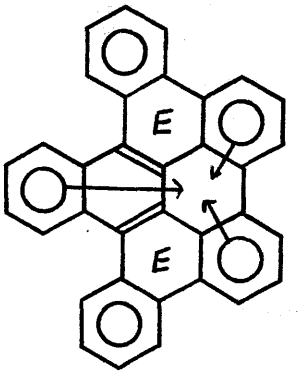
Connection of two o - phenylene complexes to triphenylene and 1.2, 3.4 - dibenzanthracene[8] gives 1.12, 2.3, 10.11 - tribenzoperylene[11] and 2.3, 10.11 - dibenzo - 1.12 - (o - phenylene) - perylene[12] respectively. The shifts associated with the formation of the four single bonds are 430 and 360 A° respectively which gives a value of 215 and 180 A° for the formation of two single bonds.





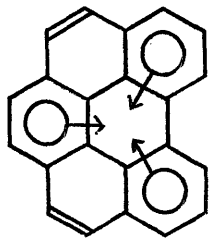
λ_β = 2570 $\xrightarrow{+430}$ 3000 A°

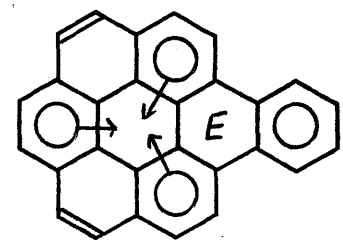




λ_β = 2900 $\xrightarrow{+360}$ 3260 A°

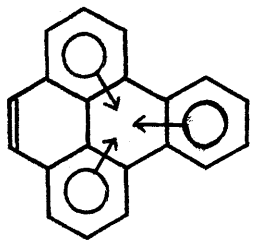
A smaller shift (170 A°) is observed in passing from 1.12 - benzoperylene[13] to 1.2 - benzocoronene.[14]

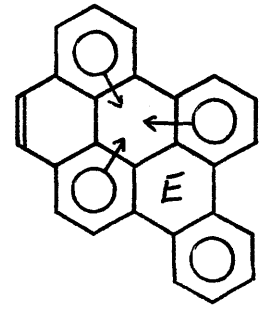


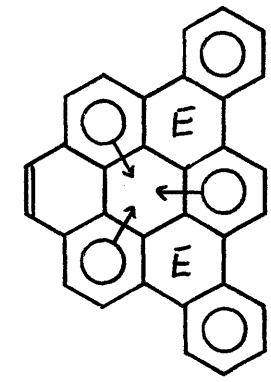


λ_β = 3030 $\xrightarrow{+170}$ 3200 A°

Similar small shifts (175 and 165 A°) are recorded in going from 1.2 - benzopyrene to 1.2 - benzo - 3.4' - (o - phenylene) - pyrene and from 1.2 - benzo - 3.4' - (o - phenylene) - pyrene to 1.2 - 5.6 - dibenzocoronene.[14]





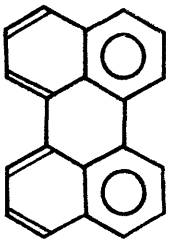


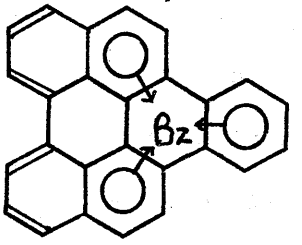
λ_β = 2920 $\xrightarrow{+175}$ 3095 $\xrightarrow{+165}$ 3260 A°

All the above examples are examples of o - phenylenation in which the observed shift is due entirely to the formation of single bonds. This shift may have a value ranging from 165 to 300 A°.

In striking contrast is the shift observed in a "benzenogenic

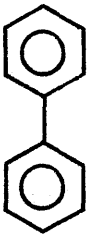
annellation", for example, in passing from perylene to 1.12 - o - phenylene-perylene. Its value (595 A°) far exceeds the value for two single bonds and an induced sextet (marked Bz.) has formed,[14]

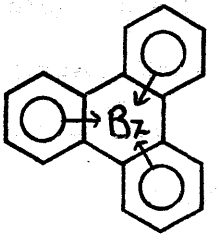




λ_β = 2510 $\xrightarrow{+590}$ 3105 A°

A similar large shift (590 A°) is recorded in going from diphenyl to triphenylene.





λ_β = 1980 $\xrightarrow{+590}$ 2570 A°

So great is the difference in value between the shifts associated with the formation of single bonds and the shifts associated with a "benzenogeric annellation" that it is not possible to confuse the two. From the magnitude of the annellation effect it is immediately possible to say whether the annellation has taken place with or without the formation of an induced sextet.

The shift associated with the tri - o - phenylenation of 2.3 - trinaphthylene (IV) is 640 A^{o}. If we assume that each annellation contributes equally, the value for the annellation of a single o - phenylene complex is 213 A^{o}. This value lies well within the range of values, 165 to 300 A^{o}, associated with the formation of single bonds only. Thus, the fusion of the three o - phenylene complexes to 2.3 - trinaphthylene has resulted in the formation of three empty rings (marked E) in formula(Ib). In this formula the central ring has induced benzenoid character (marked Bz) by virtue of the reversible transfer of three pairs of $\overline{\pi}$ - electrons from the three inherent benzenoid rings. There is also the possibility that the 2.3 - trinaphthylene complex is free to rotate or oscillate through the hexabenzocoronene system.

In the above argument in order to obtain a value for the annellation of a single o - phenylene complex to 2.3 - trinaphthylene (IV) we assumed an equal contribution from each annellation. However the shifts related to the fusion of the rings 1, 2 and 3 in formula (Ib) need not be equal. Indeed in building up coronene from triphenylene by connecting three double bonds, three very different shifts accompany the connection of the three double[14] bonds. It is not possible in the "synthesis" of hexabenzocoronene from 2.3 - trinaphthylene, to predict whether equal shifts will accompany the connection of the three o - phenylene complexes or whether the shifts which accompany o - phenylenation will follow the same pattern as those which are observed when three double bonds are connected to triphenylene forming coronene. To determine the magnitude of the individual shifts it would be necessary to synthesise the hydrocarbons

which result from the fusion of one and two o - phenylene complexes respectively to 2.3 - trinaphthylene.

Formula (Ib) for hexabenzocoronene, in which only a fraction of the rings are in aromatic conjugation accounts for the fact that the spectrum of hexabenzocoronene occurs at a shorter wavelength than would be expected from a consideration of the number of $\overline{\Pi}$ - electrons present. A similar situation exists in 1.12, 2.3, 4.5, 6.7, 8.9, 10.11 - hexabenzocoronene in which the system in aromatic conjugation is that of triphenylene the other sextets being connected to the triphenylene system by single bonds which form empty rings.[15]

1.2, 3.4, 5.6, 7.8, 9.10, 11.12 - Hexabenzocoronene (I) shows an intense red phosphorescence with emission bands at 6160 and 6270 A^{o} in a glassy frozen solution of methylcyclohexane and isopentane at 77^{o} K after irradiation. This phosphorescence spectrum is similar to that of pyrene[16] (bands at 5940 and 6050 A^{o} Figure II). This could be due to the fact that the ratio of the number of $\overline{\Pi}$ - electrons present in inherent sextets compared with the number present in double bonds is the same in both hydrocarbons. The life of phosphorescence is related to the number of inherent aromatic sextets, the greater the number of sextets the longer the life of phosphorescence. The life of the phosphorescence of hexabenzocoronene was found, as expected, to be very much longer than that of pyrene.

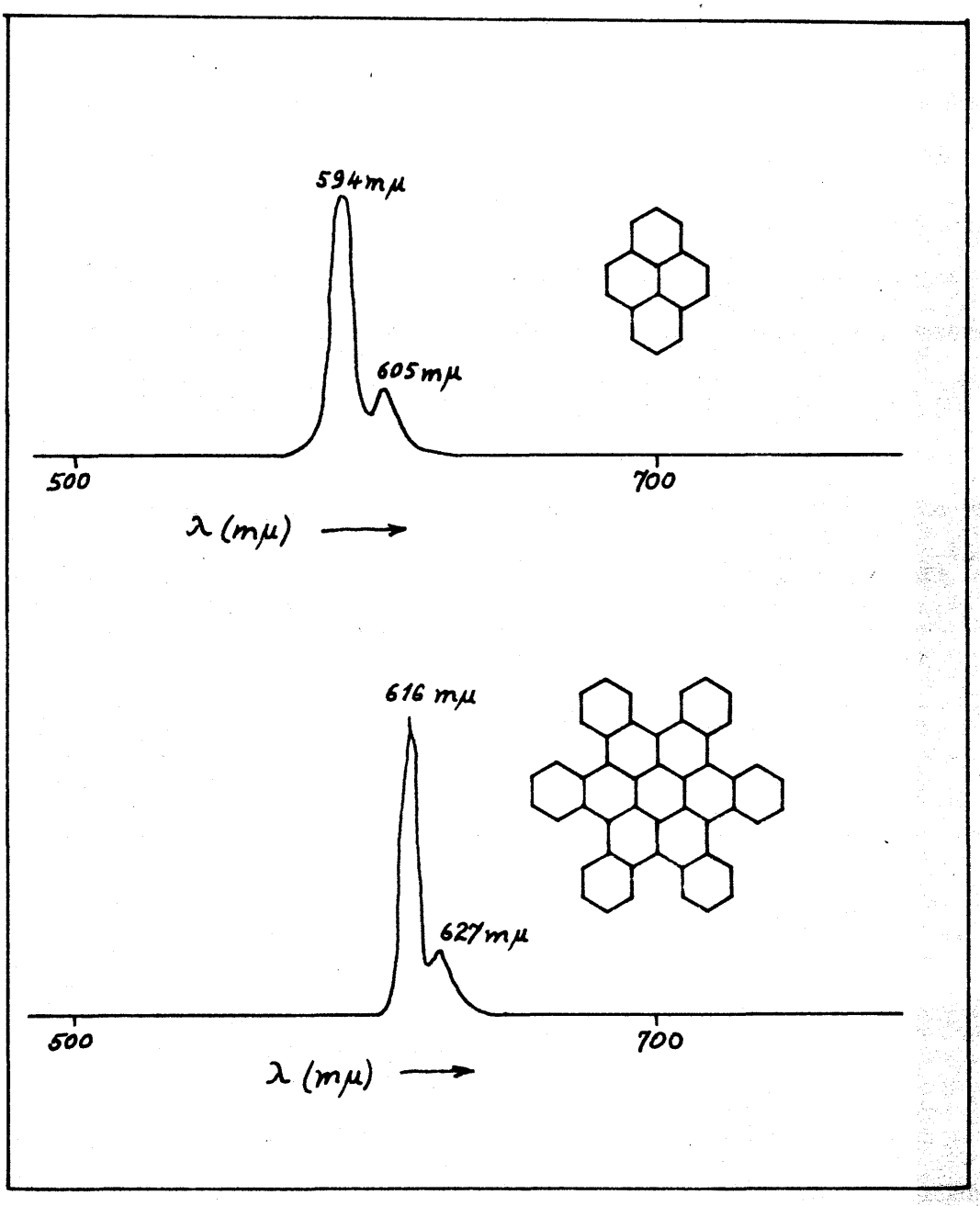
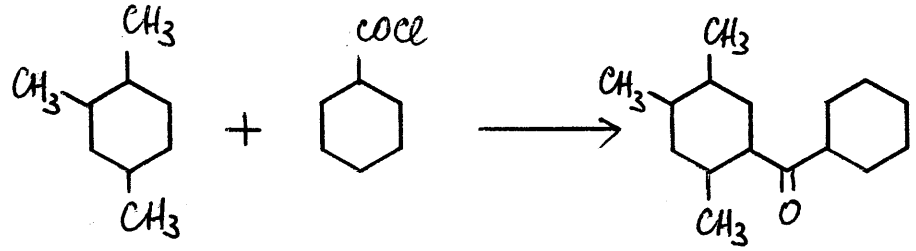
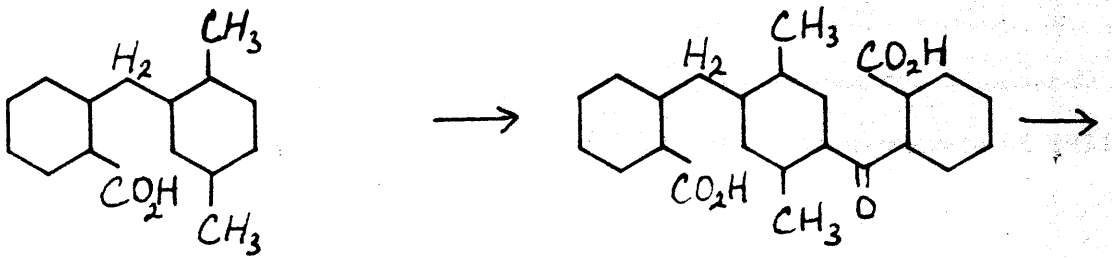


Figure 2. Phosphorescencespectra (77° K).

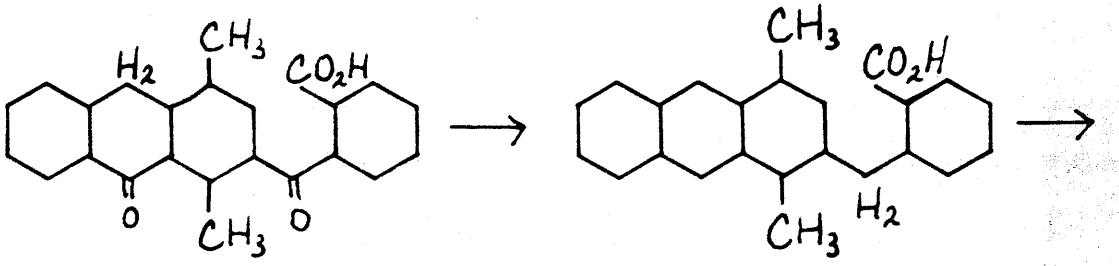
EXPERIMENTAL DISCUSSION: 1 - (o - Carboxybenzoyl) - 2.5 - dimethylbenzene[17] was reduced to 1 - (o - carboxybenzyl) - 2.5 - dimethylbenzene (V) with zinc and sodium hydroxide. When the above acid (V) was condensed with one molecule of phthalic anhydride in the presence of aluminium chloride a uniform condensation product 1 - (o - carboxylbenzyl) - 4 - (o - carboxylbenzoyl) - 2.5 - dimethylbenzene (VI) was obtained. It is assumed that condensation has taken place at position 4 by analogy with the condensation of ψ cumene with benzoyl chloride which yields 4 - benzoyl - 1, 2.5 - trimethylbenzene.[18]



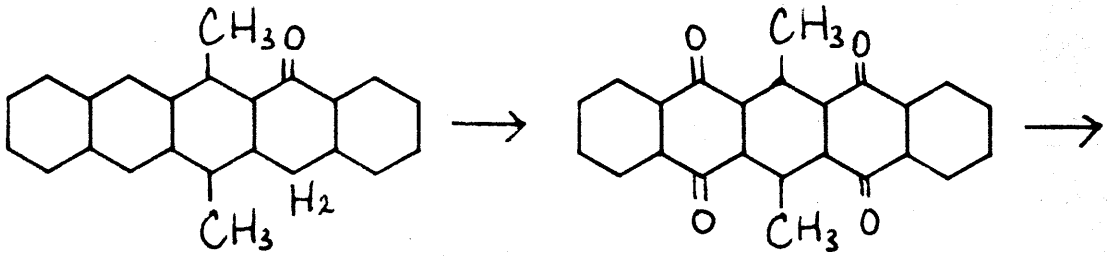
1 - (o - Carboxybenzyl) - 4 - (o - carboxybenzoyl) - 2.5 - dimethylbenzene (VI) was cyclized to 2 - (o - carboxybenzoyl) - 1.4 - dimethylanthrone - (9) (VII) with concentrated sulphuric acid. (VII) was readily oxidized and could not be obtained in a pure state. Prolonged reduction of (VII) with zinc and potassium hydroxide furnished 2 - (o - carboxybenzyl) -



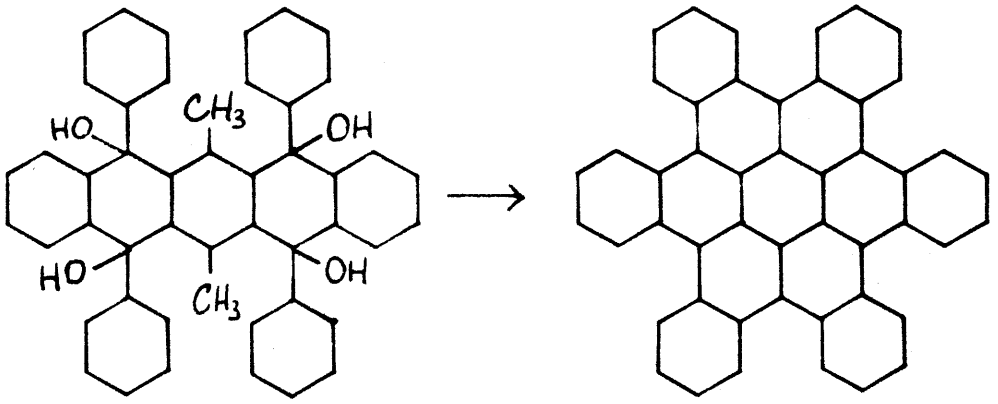
V VI



VII VIII



IX X



XI I

1.4 - dimethylanthracene (VIII). The spectrum of (VIII) is shown in (Figure III) and is that of a typical anthracene derivative. A milder reduction of (VII) with zinc and sodium hydroxide gave a mixture of (VIII) and 2 - (2' - carboxy - 1' - phenylhydroxmethyl) - 1.4 - dimethylanthracene - lactone. Ring closure of 2 - (o - carboxybenzyl) - 1.4 - dimethylanthracene (VIII) to 6.13 - dimethylpentacenone - (5) was accomplished by refluxing with phosphorus oxychloride. Excess chromic acid oxidised (IX) to 6.13 - dimethylpentacene - 5.14, 7.12 - diquinone (X), a yellow crystalline compound which gave a violet vat with alkaline sodium dithionite. When the diquinone (X) in the form of a very fine suspension in benzene was treated with an ethereal solution of phenyl lithium the tetraol (XI) was formed. Pyrolysis of this tetraol (XI) with copper powder at 400° gave 1.2, 3.4, 5.6, 7.8, 9.10, 11.12 - hexabenzocoronene (I) which was extracted from the copper with xylene and purified by chromatography.

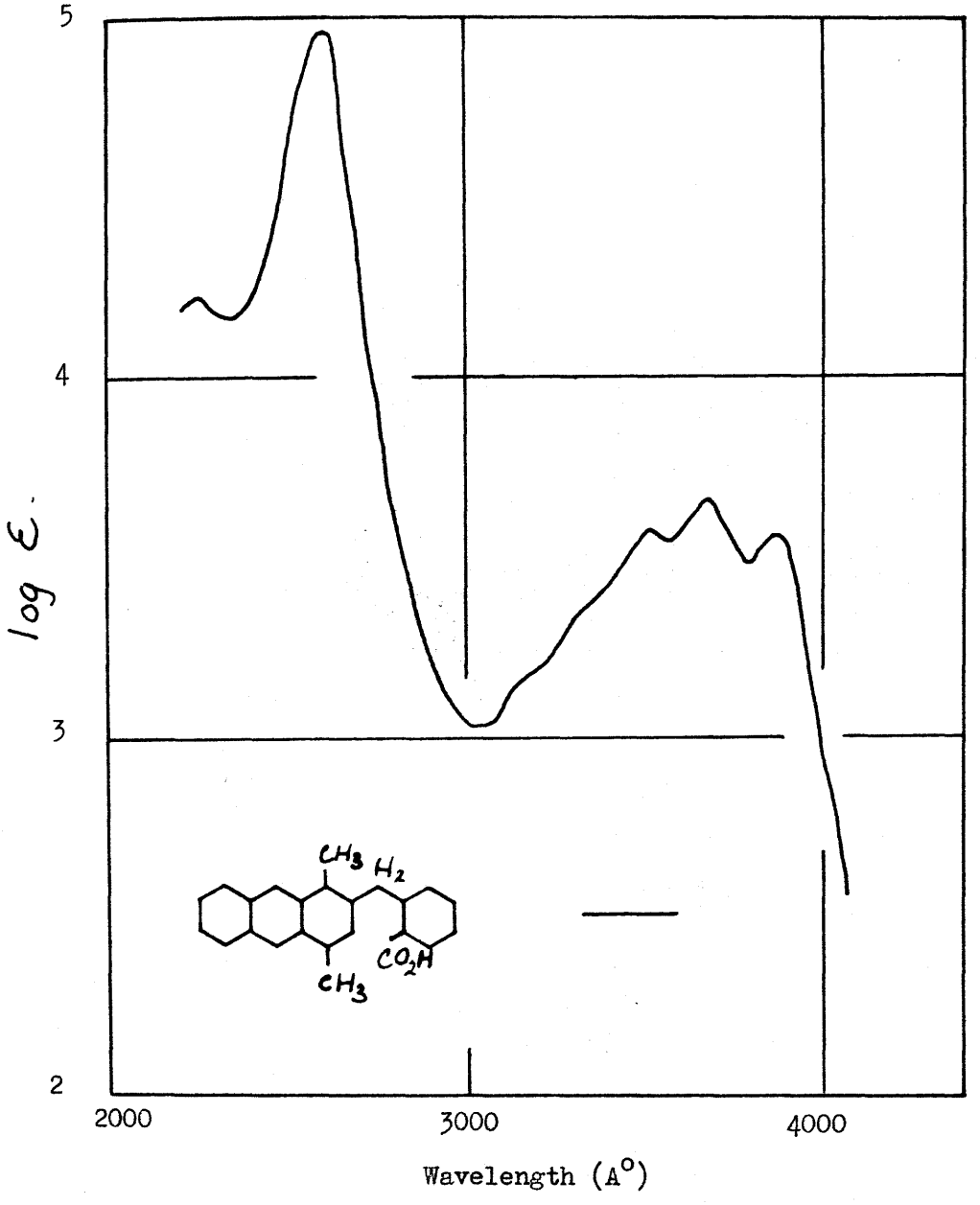


Figure 3. Absorption max. (A°) and log ε (in parentheses). Potassium salt of 2 - (o - carboxybenzyl) - 1.4 - dimethylanthracene in water, p: 3860 (3.56), 3670 (3.66), 3400 (3.58); β : 2600 (4.97), 2260 (4.24).

EXPERIMENTAL

1 - (o - Carboxybenzyl) - 2.5 - dimethylbenzene (V).

1 - (o - Carboxybenzoyl) - 2.5 - dimethylbenzene (50g) was reduced with copper activated zinc dust (75g) and aqueous sodium hydroxide (8%, 1500 ml) by refluxing for 3½ days. Zinc dust (75g) was added in portions (3 x 25g) at intervals of 24 hours. The hot alkaline solution was filtered from excess zinc, acidified with concentrated hydrochloric acid and the precipitated acid (41g) crystallized from benzene. A second crystallization from pet. ether 60 - 80° gave 1 - (o - carboxybenzyl) - 2.5 - dimethylbenzene (V) as colourless needles, m.p. 130 - 132°. (V) dissolves in concentrated sulphuric acid to give a yellow solution.

Found: C, 80.3; H, 6.9.

$C_{16}H_{16}O_2$ requires: C, 80.0; H, 6.7%.

1 - (o - Carboxybenzyl) - 4 - (o - carboxybenzoyl) - 2.5 - dimethylbenzene (VI).

Powdered 1 - (o - carboxybenzyl) - 2.5 - dimethylbenzene (V) (26g) was added to a suspension of finely ground aluminium chloride (64g) and phthalic anhydride (17.7g) in tetrachloroethane (78 ml). The solution became yellow and hydrogen chloride was evolved. After 5 minutes at room temperature the reaction vessel was immersed in a water bath at 60°. A vigorous evolution of hydrogen chloride occurred and the solution became wine red in colour. When the evolution of hydrogen chloride had ceased (25 minutes) the viscous red complex was decomposed with dilute hydrochloric acid and the precipitated condensation product (31g) was filtered off and washed with benzene and hot water. Crystallization from glacial acetic acid furnished 1 - (o - carboxybenzyl) - 4 - (o - carboxybenzoyl) - 2.5 - dimethylbenzene (VI) as clusters of colourless needles, m.p. 249 - 250° which dissolve in concentrated sulphuric acid to give a yellow solution which rapidly changes to orange and then to red on standing.

Found: C, 74.15; H, 5.2.

$C_{24}H_{20}O_5$ requires: C, 74.2 ; H, 5.2%.

2 - (o - Carboxybenzoyl) - 1.4 - dimethylanthrone - (9)(VII).

Finely divided 1 - (o - carboxybenzyl) - 4 - (o - carboxybenzoyl) - 2.5 - dimethylbenzene (VI) (33g) was added with stirring to concentrated sulphuric acid (250 ml) and the mixture was heated at 80° for 5 minutes.

The solution initially orange-red in colour became brown. The cold mixture was poured onto ice and the crude cyclization product (VII) (28g) was filtered off and washed with water. (VII) was readily oxidized, could not be obtained in a pure state and was used in the crude form for the next stage.

2 - (o - Carboxybenzyl) - 1.4 - dimethylanthracene (VIII).

Crude 2 - (o - Carboxybenzoyl) - 1.4 - dimethylanthrone - (9) (VII) (48g) was dissolved in aqueous potassium hydroxide (5%, 2500 ml), zinc dust (70g) added and the mixture heated under reflux. The initial dark red colour was rapidly discharged and a yellow solution resulted. Reduction was prolonged for 5 days and an additional 120g of zinc dust was added in portions (4 x 30g) at intervals of 24 hours. The alkaline solution was filtered hot from excess zinc and acidified with concentrated hydrochloric acid. The zinc dust was destroyed with concentrated hydrochloric acid and the residue was combined with the above precipitated acid to give crude 2 - (o - carboxybenzyl) - 1.4 - dimethylanthracene (VIII) (36g). (VIII) crystallized from xylene in small yellow needles, m.p. 243 - 244° and dissolves in concentrated sulphuric acid to give an orange solution which changes to brown-green and finally to green on standing.

Found: C, 84.8; H, 6.3.

$C_{24}H_{20}O_2$ requires: C, 84.7; H, 5.9%.

6.13 - Dimethylpentacenone - (5) (IX).

The above carboxylic acid (VIII) (20g) was dissolved in phosphorus oxychloride (400 ml) and the mixture heated under reflux for 5 minutes. Phosphorus oxychloride (300 ml) was distilled off, xylene (300 ml) added and the mixture redistilled until about (300 ml) of distillate was obtained. The mixture still contained phosphorus oxychloride and was poured into water and the xylene steam distilled off. Crystallization of the material thus obtained from xylene gave 6.13 - dimethylpentacenone - (5) (IX) (8.6g) as golden brown ferns, m.p. 268 - 270°. (IX) dissolves in concentrated sulphuric acid to give a green colour.

Found: C, 89.7; H, 5.8.

$C_{24}H_{18}O$ requires: C, 89.4; H, 5.6%.

6.13 - Dimethylpentacene - 5.14, 7.12 - diquinone (X).

Finely powdered 6.13 - dimethylpentacenone - (5) (IX) (10g) was suspended in hot glacial acetic acid (300 ml) and chromic acid (21g) was added rapidly so that the mixture refluxed vigorously. (IX) dissolved and the diquinone (X) began to precipitate from the boiling solution. Refluxing was continued for a further 30 minutes when the precipitated diquinone (X) (7.8g) was filtered off and washed with acetic acid and water. Dilution of the acetic acid mother liquor with water furnished an additional 450 mg of (X). 6.13 - dimethylpentacene - 5.14, 7.12 - diquinone crystallizes in large green-yellow needles from 1.2.4 - trichlorobenzene which darken at 300° and melt at 320 - 322° with dec. (X) gives a violet vat

with alkaline sodium dithionite and dissolves in concentrated sulphuric acid to give a yellow solution which changes to orange and then to green on standing.

Found: C, 78.7; H, 4.1.

$C_{24}H_{14}O_4$ requires: C, 78.7; H, 3.85%.

5.7.12.14 - Tetraphenyl - 5.7.12.14 - tetrahydroxy - 5.7.12.14 - tetrahydro - 6.13 - dimethylpentacene (XI).

Bromobenzene (25.84g) was added to strips of lithium metal (2.3g) suspended in dry ether (200 ml) in an atmosphere of nitrogen and the mixture was refluxed until all the lithium had reacted (2 - 3 hours). The ethereal solution was then filtered through glass wool into a suspension of very finely divided 6.13 - dimethylpentacene - 5.14, 7.12 - diquinone in dry benzene, prepared by shaking the diquinone (10g), a handful of glass beads and dry benzene (200 ml) in a thick walled glass bottle for 12 hours. The bottle was securely corked and the mixture was shaken for 48 hours. The brown colour which developed immediately changed to red as the reaction proceeded. Decomposition with ice and dilute aqueous acetic acid gave a violet-brown product which was washed with ether. The ether insoluble material (3g) was filtered off given a washing with pyridine, and the pyridine mother liquor decanted leaving behind unchanged diquinone (X) (2.05g). Dilution of the pyridine mother liquor with water gave crude tetraol (XI) (500 mg). Slow evaporation of the ether from the ether washing furnished after 7 days (1.02g) of crude tetraol. No more crystallization took place

from the ether and the ether was replaced with benzene and pet. ether 100 - 120° added to the hot benzene solution. In this way an additional 4.5g of tetraol were obtained. Total yield (6.02g). Repeated crystallization from acetone ethyl acetate mixture gave the tetraol as colourless needles, m.p. 312 - 318° dec. which dissolve in concentrated sulphuric acid to give a violet solution.

Found: C, 84.4; H, 5.6.

$C_{48}H_{38}O_4$ requires: C, 84.9; H, 5.65%.

1.2, 3.4, 5.6, 7.8, 9.10, 11.12 - Hexabenzocoronene (I).

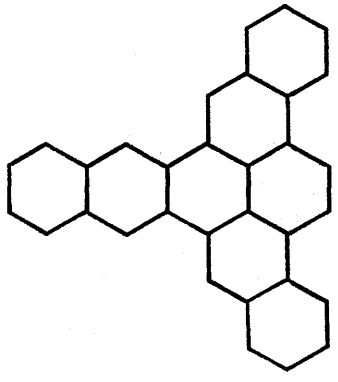
An intimate mixture of the above tetraol (XI) (1g) and copper powder was pyrolysed in an atmosphere of carbon dioxide at 400 - 440° for 2 hours. The copper was extracted with xylene and the extract chromatographed on alumina grade I. Eluting with xylene gave a yellow-red eluate which yielded small yellow prisms of hexabenzocoronene (I) (20 mg), m.p. 516° dec. (I) dissolves slowly in concentrated sulphuric acid to give a green solution which changes to brown on standing.

Found: C, 95.6; H, 4.2.

$C_{48}H_{24}$ requires: C, 96.0; H, 4.0%.

C H A P T E R IV.

4.5, 8.9 - DIBENZO - NAPHTHO - (2'''.3''' - 1.2) - PYRENE and 3.4, 9.10 - DIBENZO - NAPHTHO - (2'''.3''' - 1.2) - PYRENE.



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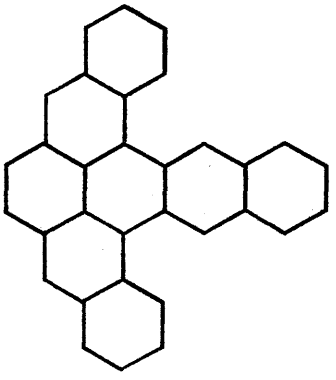
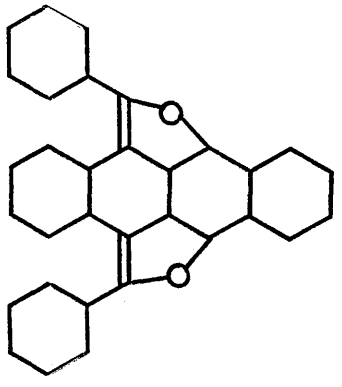


II

INTRODUCTION: 4.5, 8.9 - Dibenzo - naphtho - (2'''.3''' - 1.2) - pyrene (I) and 3.4, 9.10 - dibenzo - naphtho (2'''.3''' - 1.2) - pyrene (II) were synthesised to complete the two

series; 3.4, 9.10 - dibenzopyrene,[1] 1.2, 4.5, 8.9 - tribenzopyrene[2] and 4.5, 8.9 - dibenzo - naphtho - (2'''.3''' - 1.2) - pyrene (I) and the series 3.4, 9.10 - dibenzopyrene, 1.2, 3.4, 9.10 - tribenzopyrene[3] and 3.4, 9.10 - dibenzo - naphtho - (2'''.3''' - 1.2) - pyrene (II) and thus enable a comparative study to be made of the effect of fusing one and two rings to the 1.2 and 6.7 double bonds of 3.4, 9.10 - dibenzopyrene.

Recently two unsuccessful syntheses of 4.5, 8.9 - dibenzo - naphtho - (2'''.3''' - 1.2) - pyrene have been reported.[4] The first synthesis a Friedel - Crafts reaction between picene and naphthalene in the presence of aluminium chloride yielded no useful product, while the second synthesis the cyclization of the dioxido compound (III) in an aluminium chloride melt gave only fission products of (III). In the present chapter the synthesis of (I) from 3.4, 9.10 - dibenzopyrene and o - toluyl chloride is described.

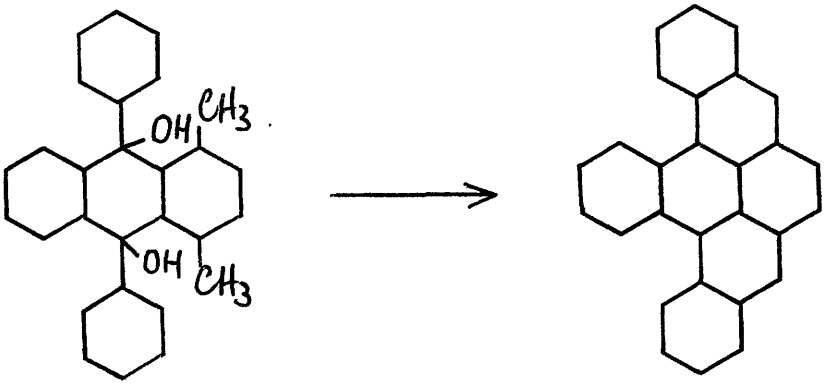


III

$\longrightarrow$ fission products

9.10 - Diphenyl - 9.10 - dihydroxy - 9.10 - dihydro - 1.4 - dimethylanthracene (IV) is dehydrated and cyclodehydrogenated to 1.2, 3.4,

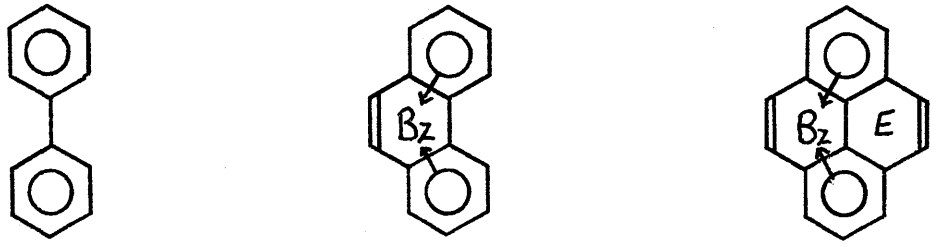
9.10 - tribenzopyrene[3] when heated with copper powder at 400°.



(IV)

In the synthesis of 3.4, 9.10 - dibenzo - naphtho - (2'''.3''' - 1.2) - pyrene it was hoped to exploit this reaction and obtain (II) by a similar dehydration and cyclodehydrogenation of 5.12 - diphenyl - 5.12 - dihydroxy-5.12 - dihydro - 1.4 - dimethyltetracene.

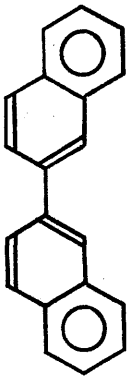
THEORETICAL DISCUSSION: Pyrene can be derived from diphenyl by fusing two ethylene bridges forming firstly phenanthrene and then pyrene.



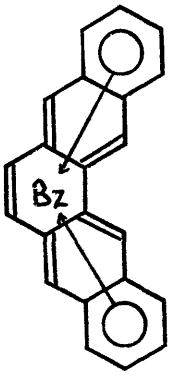
λ_β = 2100 $\xrightarrow{+430}$ 2530 $\xrightarrow{+210}$ 2740 A°

The annellation effect is very asymmetric and hence one of the central rings must have induced benzenoid character (Bz) while the other ring is empty (E).

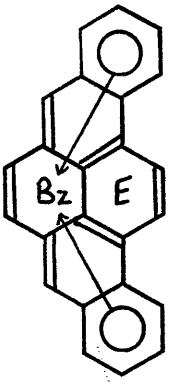
3.4, 9.10 - Dibenzopyrene can be derived in a similar way from 2.2' - dinaphthyl (V). However two different hydrocarbons may result from the fusion of the first ethylene bridge, the structure of the first hydrocarbon depending on the points of attachment of the ethylene bridge. Connection of the first ethylene bridge across the 3.3' positions gives pentaphene (VI) and the annellation series, 2.2' - dinaphthyl, pentaphene and 3.4, 9.10 - dibenzopyrene.



V



VI

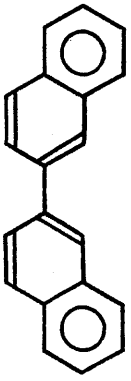


VII

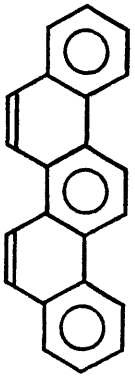
λ_β = 2550 $\xrightarrow{+595}$ 3145 $\xrightarrow{+175}$ 3320 A°

The observed shifts are (595 and 175 A° respectively). The second shift is asymmetric and hence during the first annellation an induced benzenoid ring (Bz) is formed while the second annellation produces an empty ring (E).

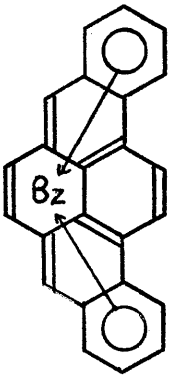
On the other hand connection of the first ethylene bridge across the 1.1' positions gives picene (VIII) and the annellation series, 2.2' - dinaphthyl, picene and 3.4, 9.10 - dibenzopyrene.



V



VIII



VII

λ_β = 2550 $\xrightarrow{+295}$ 2845 $\xrightarrow{+475}$ 3320 A°

The first shift (295 A°) is small and the newly formed ring in picene does not have induced benzenoid character. The second shift (475 A°) is large and the second annellation produces an induced benzenoid ring (Bz).

The isomeric hydrocarbons pentaphene (VI) and picene (VIII) represent two distinct ways of conjugating eleven double bonds within the framework of five fused hexagonal rings. The fact that 3.4, 9.10 - dibenzopyrene can be derived from both pentaphene and picene by annellating an ethylene bridge suggests that the two distinct types of conjugation existing in pentaphene and picene are also present in 3.4, 9.10 - dibenzopyrene. If this is so then the spectrum of 3.4, 9.10 - dibenzopyrene (Figure I) should represent a superposition of the spectra of pentaphene and picene. The spectrum of 3.4, 9.10 - dibenzopyrene shows a β - band at 3320 Å and a β' band at 2970 A° and these bands are shifted 175 and 125 A° respectively from the β - band of pentaphene (3145 A°) and that of picene (2845 A°). These shifts are due to the single bonds of the ethylene bridge.

1.2, 4.5, 8.9 - Tribenzopyrene (IX) (Spectrum Figure IV) can be built up from picene (VIII) by connecting an o - phenylene complex and from 3.4, 9.10 - dibenzopyrene (VII) by fusing a butadiene complex to the 6.7 double bond. Consider firstly the former annellation, the annellation effect is 105 A° and is well below the maximum value related to the formation of single bonds only.

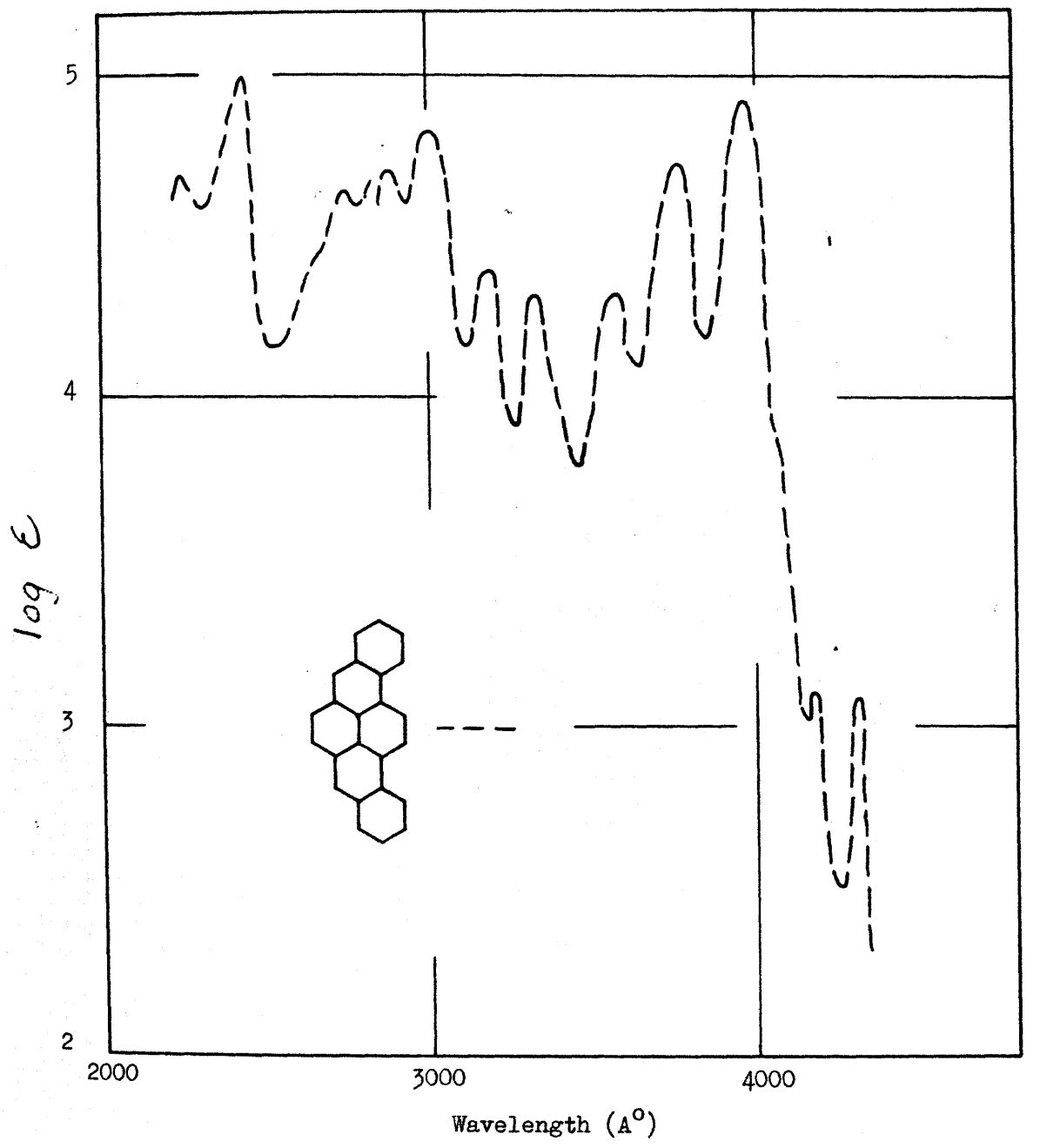
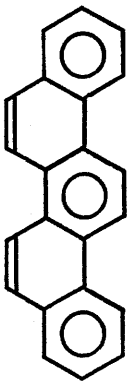
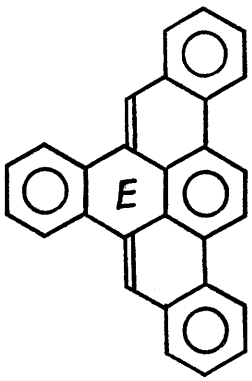


Figure 1. Absorption max. (A°) and log ε (in parentheses). 3.4, 9.10 - Dibenzopyrene in benzene, α : 4330 (3.10), 4190 (3.12); p: 3970 (4.92), 3750 (4.72), 3565 (4.32); β : 3320 (4.32), 3170 (4.40); β' : 2970 (4.82) 2850 (4.70); in alcohol, β'': 2720 (4.64), 2420 (4.98), 2220 (4.68).



(VIII)



(IX)

λ_{β} = 2845 $\xrightarrow{+105}$ 2950 A°

Hence the newly formed ring must be empty (E). If there is an empty ring (E) in 1.2, 4.5, 8.9 - tribenzopyrene (IX) then there must also be an empty ring at this position in 3.4, 9.10 - dibenzopyrene (VIIa) since 1.2, 4.5, 8.9 - tribenzopyrene is derived from dibenzopyrene simply by fusing a butadiene complex to the 6.7 double bond. The presence of an empty ring at this position in dibenzopyrene determines the conjugation type (picene type) and fixes the 6.7 double bond. Consequently the shift associated with the fusion of the butadiene complex to the 6.7 double bond should be small - the shift associated with annellation to a fixed double bond.[5] The observed shift β' Dibenzopyrene $\longrightarrow \beta$ Tribenzopyrene is in fact -20 A°.

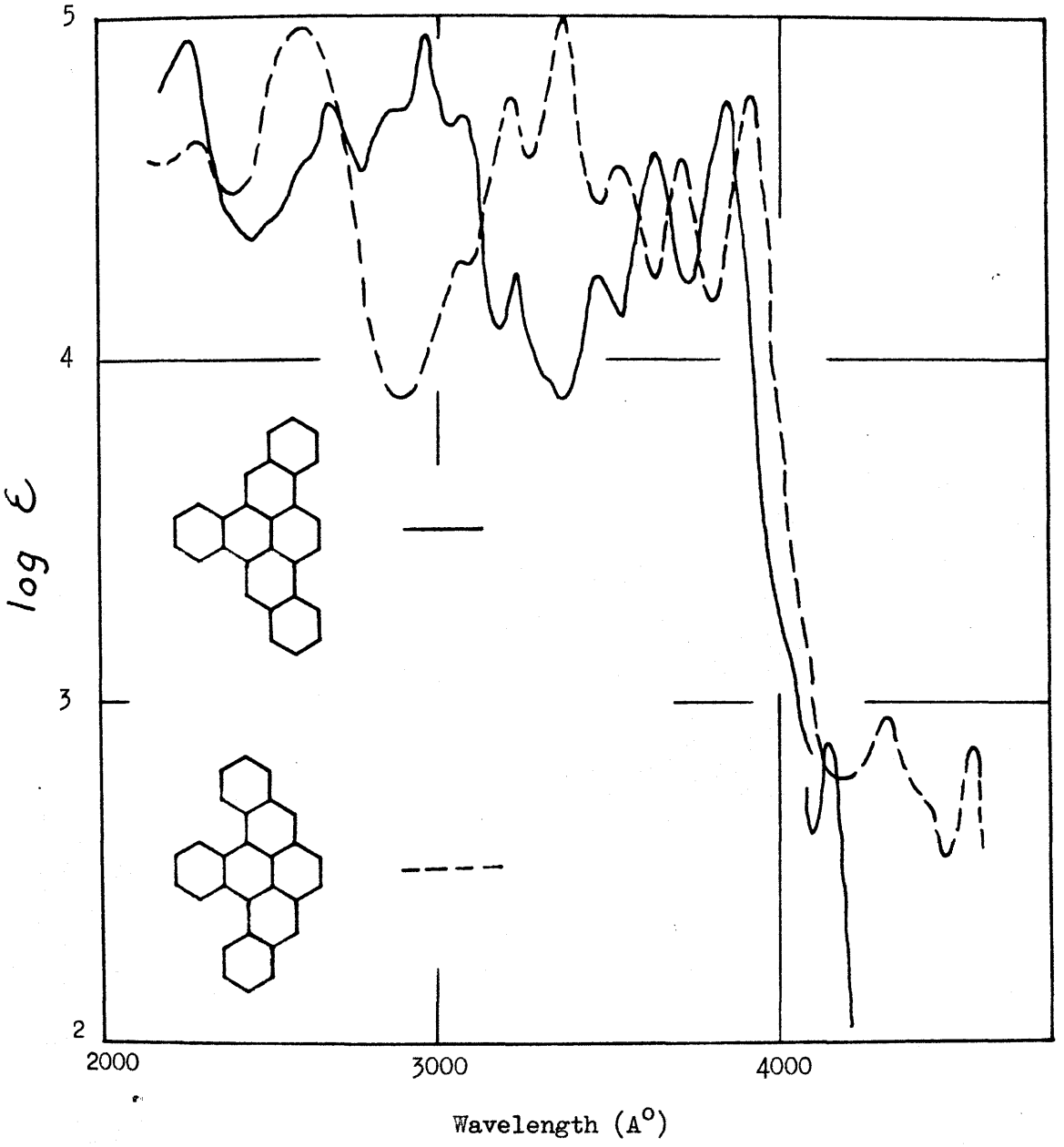
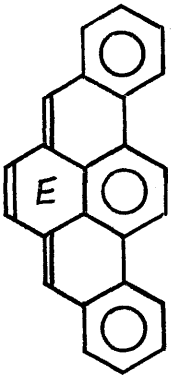
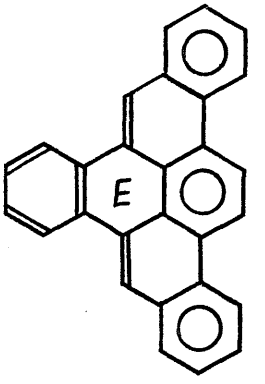


Figure 4. Absorption max. (A°) and log ε (in parentheses). 1.2, 4.5, 8.9 - Tribenzopyrene in benzene, α : 4180 (2.86); p: 3850 (4.76), 3640 (4.60), 3465 (4.25); β : 3230 (4.26), 3070 (4.70), 2965 (4.94), 2850 (4.70); β': 2680 (4.73); β'': 2260 (4.92). 1.2, 3.4, 9.10 - Tribenzopyrene in alcohol, α : 4610 (2.86), 4340 (2.94); p: 3930 (4.74), 3730 (4.56), 3540 (4.54); β : 3375 (4.98), 3220 (4.74); β': 2600 (4.94), 2290 (4.62).



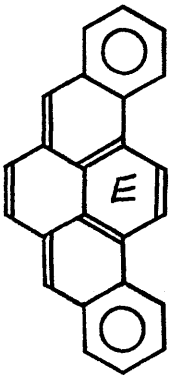
VIIa



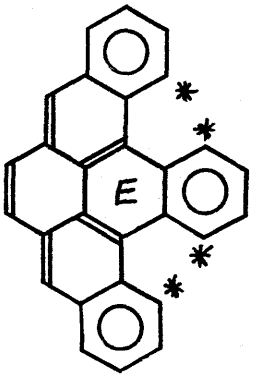
(IX)

$\lambda_{\beta'}$ = 2970 $\xrightarrow{-20}$ 2950 A°

The shift in the β- bands in going from 3.4, 9.10 - dibenzopyrene to 1.2, 3.4, 9.10 - tribenzopyrene (X) (Spectrum Figure IV) is + 55 A°.



VIIb



X

λ_{β} = 3320 $\xrightarrow{+55}$ 3375 A°

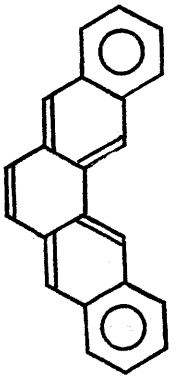
$\xrightarrow{-85}$ -140

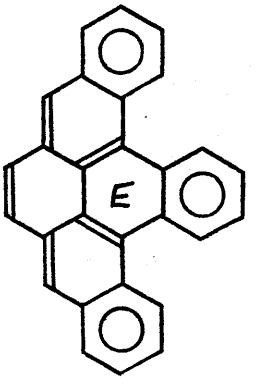
3235 corrected

However to measure this shift correctly the β- band of 1.2, 3.4, 9.10 - tribenzopyrene must be corrected to account for the overlapping hydrogen

atoms (marked *) which shift the β - band to the red.[5] Applying a minimum correction of -140 A° the corrected β - band is 3235 A° and the shift in going from dibenzopyrene to tribenzopyrene is -85 A°. Now very small positive or negative shifts are an indication of fixed double bonds at the positions where the new rings have been fused.[5] Thus the 1.2 double bond of 3.4, 9.10 - dibenzopyrene is fixed and conjugation is of the pentaphene type in both 3.4, 9.10 - dibenzopyrene (VIIb) and tribenzopyrene (X).

Building up tribenzopyrene from pentaphene by o - phenylenation provides further support for formula (X) for tribenzopyrene.

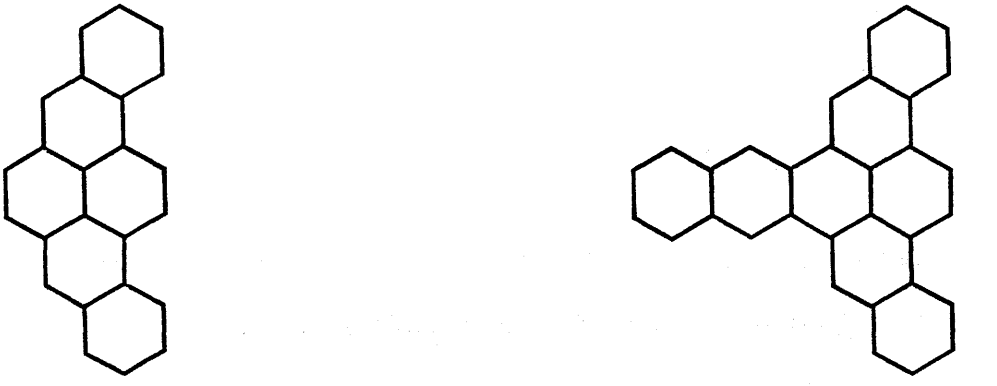




λ_β = 3145 $\xrightarrow{+90}$ 3235 A°

The shift is small (+90 A°) and accounts for the formation of single bonds only and the newly formed ring must be empty (E). Small shifts of both the β and β' - bands (120 and 10 A° respectively) are recorded in passing from 3.4, 9.10 - dibenzopyrene to 4.5, 8.9 - dibenzo - naphtho - (2'''.3''' - 1.2) - pyrene. If the β and β' - bands of 3.4, 9.10 -

dibenzopyrene originate from conjugation of the pentaphene and picene types respectively then both the above types of conjugation are present in 4.5, 8.9 - dibenzonaphtho - (2'''.3''' - 1.2) - pyrene.

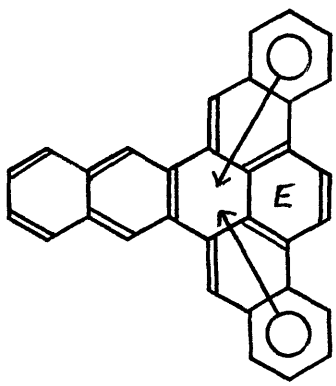


I

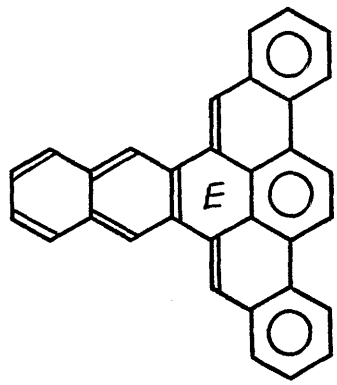
λ_{β} = 3320 $\xrightarrow{+120}$ 3440 A°

$\lambda_{\beta'}$ = 2970 $\xrightarrow{+10}$ 2980 A°

The shift in the β - band is the shift due to the extension of the pentaphene system to that of 2.3 - trinaphthylene. This is a pure annellation effect since the double bond in the central ring (Ia) drawn in to participate in the formation of an induced sextet cuts off the third branch from aromatic conjugation. The shift in the β' - band is also a pure annellation effect, the shift due to annellation to a fixed double bond (Ib).

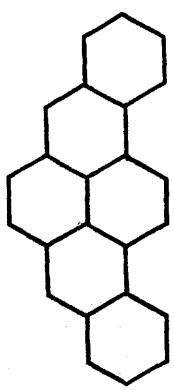


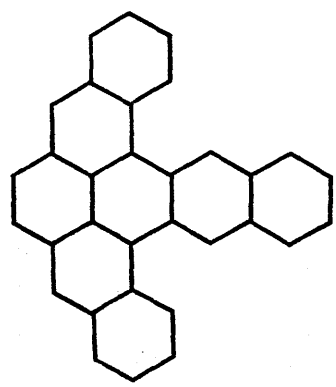
Ia.



Ib.

Shifts of -240 and -230 A° are recorded for the β and β' - bands respectively in passing from 3.4, 9.10 - dibenzopyrene to 3.4, 9.10 - dibenzo - naphtho - (2'''.3''' - 1.2) - pyrene. It is not possible to correlate these shifts with conjugation of either the pentaphene or picene types, therefore, some different type of conjugation must exist in 3.4, 9.10 - dibenzo - naphtho - (2'''.3''' - 1.2) - pyrene.





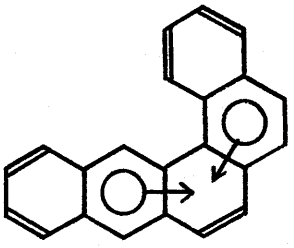
II

λ_{β} = 3320 $\xrightarrow{-240}$ 3080 A°

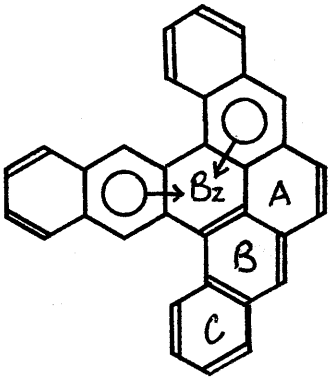
$\lambda_{\beta'}$ = 2970 $\xrightarrow{-230}$ 2740 A°

If the type of conjugation in 3.4, 9.10 - dibenzo - naphtho - (2'''.3''' -

1.2) - pyrene is of the 1.2 - benzotetraphene type (XI)[6] then the β - band of 3.4, 9.10 - dibenzo - naphtho - (2'''.3''' - 1.2) - pyrene will only be slightly shifted from the β - band of 1.2 - benzotetraphene since the double bond in the induced benzenoid ring (Bz) (II) will cut off the other rings, A, B and C from aromatic conjugation.



XI



II

λ_{β} = 3080

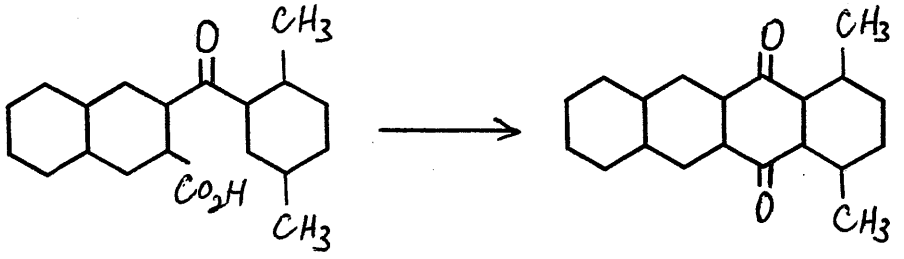
3080 A°

In fact the β - bands of 1.2 - benzotetraphene (XI) and 3.4, 9.10 - dibenzo - naphtho - (2'''.3''' - 1.2) - pyrene are identical, occurring at 3080 A° and this fact supports the view that the system in aromatic conjugation in 3.4, 9.10 - dibenzo - naphtho - (2'''.3''' - 1.2) - pyrene is the 1.2 - benzotetraphene system.

In the above discussion it is suggested that two different types of conjugation exist in 3.4, 9.10 - dibenzopyrene, conjugation of the pentaphene and picene types and that the β and β' - bands of 3.4, 9.10 - dibenzopyrene originate from conjugation of the pentaphene and picene types respectively. The effect of annellating a butadiene complex

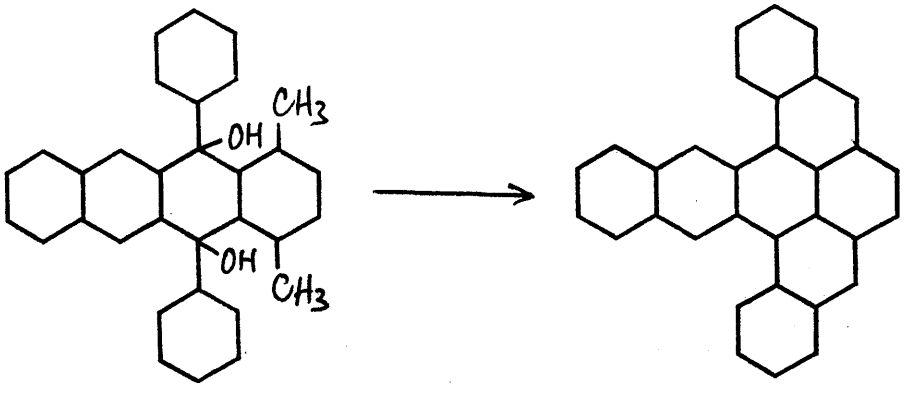
to the 1.2 and 6.7 double bonds of 3.4, 9.10 - dibenzopyrene has been studied. The former annellation gives 1.2, 4.5, 8.9 - tribenzopyrene in which conjugation has been shown to be of the picene type, the latter annellation 1.2, 3.4, 9.10 - tribenzopyrene in which conjugation is of the pentaphene type. Passing to 4.5, 8.9 - dibenzo - naphtho - (2'''.3''' - 1.2) - pyrene we witness the reappearance of both the pentaphene and picene types of conjugation, while in the isomeric 3.4, 9.10 - dibenzo - naphtho - (2'''.3''' - 1.2) - pyrene a complete departure from conjugation of the pentaphene and picene types is observed and conjugation of the 1.2 benzotetraphene type is proposed for 3.4, 9.10 - dibenzo - naphtho - (2'''.3''' - 1.2) - pyrene.

EXPERIMENTAL DISCUSSION: Numerous tetracene derivatives have been prepared from naphthalene - 2.3 - dicarboxylic anhydride and various benzene derivatives.[7] In the present synthesis the benzene derivative employed was p - xylene and the Friedel - Crafts reaction with naphthalene - 2.3 - dicarboxylic anhydride gave 2 - (3' - carboxy - 2' - naphthoyl) - 1.4 - dimethybenzene (XII) in excellent yield. This keto-acid was ring closed to 1.4 - dimethyltetracene - 5.12 - quinone with concentrated sulphuric acid at 100 - 110°.



(XII) (XIII)

The quinone (XIII) reacted with phenyl lithium to give the diol (XIV) which was pyrolysed with copper powder at 400°. At this temperature the diol was dehydrated and cyclodehydrogenated to 3.4, 9.10 - dibenzo - naphtho - (2'''.3''' - 1.2) - pyrene (II) which was purified by chromatography.



XIV II

The absorption spectrum of 3.4, 9.10 - dibenzo - naphtho - (2'''.3''' - 1.2) - pyrene (II) is shown in Figure II.

From a consideration of the structure of 3.4, 9.10 - dibenzo-pyrene (VII) it appears that the most likely positions at which mono-substitution will occur are the 5 and 6-positions. The fact that di-substitution - nitration with nitric acid in nitrobenzene and chlor-ination with sulphuryl chloride - gives the 5.8 - disubstitution product[8] suggests that monosubstitution will favour position 5.

The Friedel - Crafts reaction between 3.4, 9.10 - dibenzo-pyrene, o - toluyl chloride and aluminium chloride was conducted in methylene chloride and after the usual decomposition the crude ketone was chromatographed on alumina. Two fractions were eluted, unreacted 3.4, 9.10 - dibenzopyrene and an oil which could not be crystallized. The crude ketone was pyrolysed at 400° and the pyrolysate sublimed in vacuo.

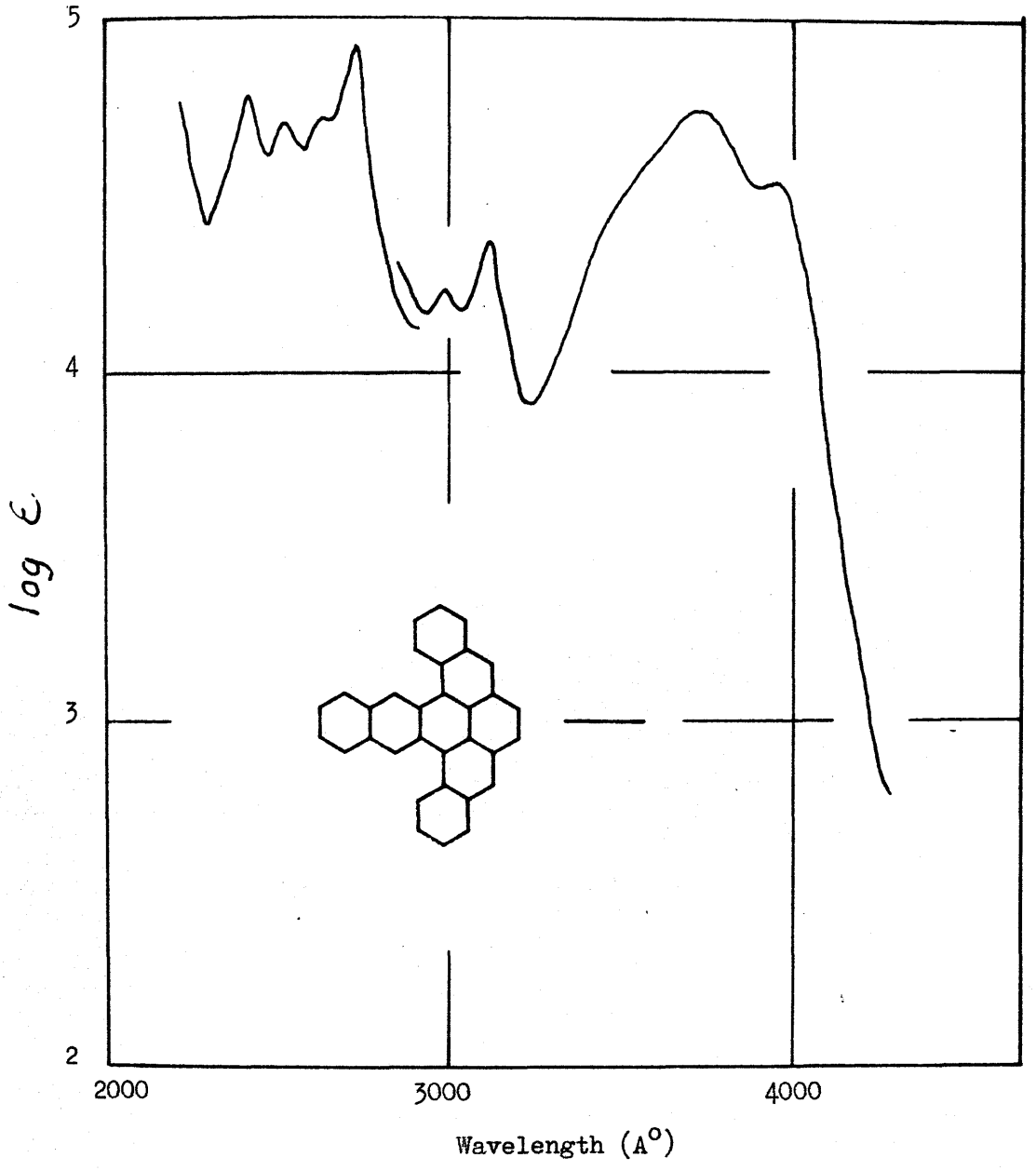
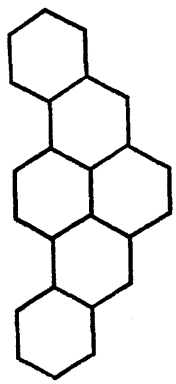
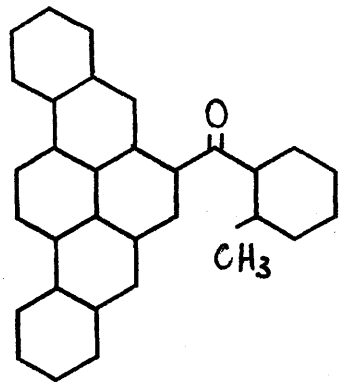


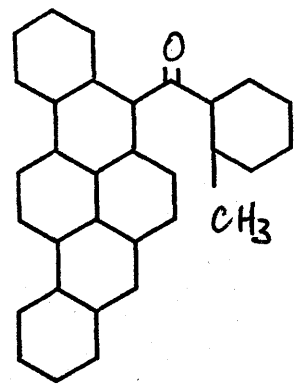
Figure 2: Absorption max. (A°) and log ε (in parentheses). 3.4, 9.10 - Dibenzo - naphtho - (2'''.3''' - 1.2) - pyrene in benzene, p: 3950 (4.54), 3730 (4.74); β: 3120 (4.37), 2990 (4.22); in alcohol, β': 2740 (4.94), 2640 (4.73), 2530 (4.72), 2420 (4.80).



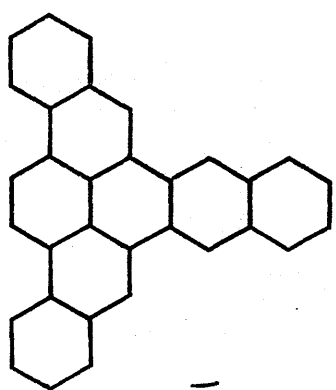
VII



XV



XVI



I

3.4, 9.10 Dibenzopyrene sublimed and was followed at a higher temperature by 4.5, 8.9 - dibenzo - naphtho - (2'''.3''' - 1.2) - pyrene which was purified by chromatography. The spectrum of (I) is recorded in Figure III. 4.5, 8.9 - Dibenzo - naphtho - (2'''.3''' - 1.2) - pyrene (I) is the product of a normal Elbs cyclization of 6 - (o - toluyl) - 3.4, 9.10 - dibenzopyrene (XV). If 5 - (o - toluyl) - 3.4, 9.10 - dibenzopyrene (XVI) is the product of the Friedel - Crafts reaction between o - toluyl chloride and 3.4, 9.10 - dibenzopyrene then the formation of (I) from 5 - (o - toluyl) - 3.4, 9.10 - dibenzopyrene (XVI),

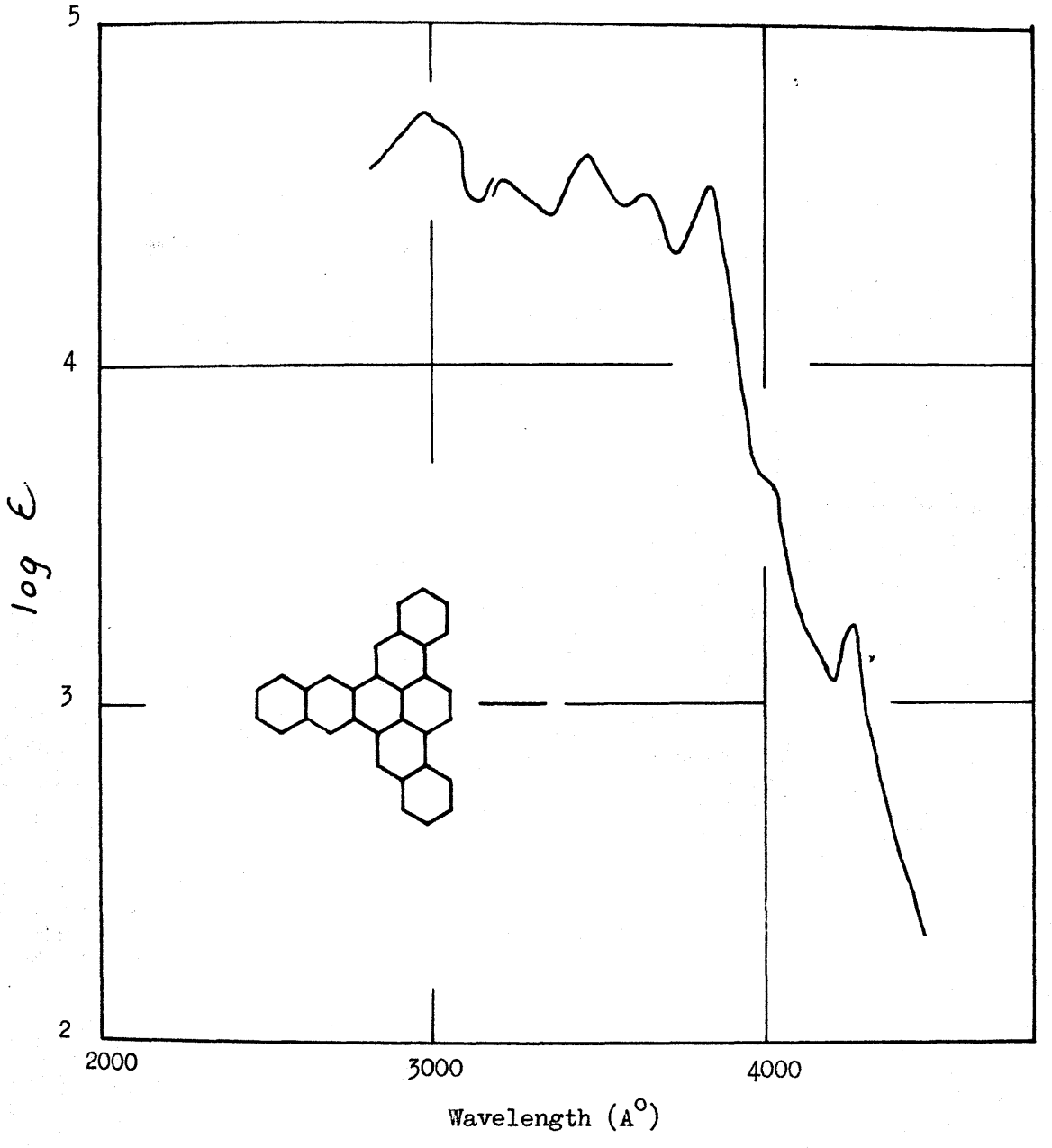


Figure 3. Absorption max (A°) and log ε (in parentheses), 4.5, 8.9 - Dibenzo - naphtho - (2'''.3''' - 1.2) - pyrene in 1.2.4. - trichlorobenzene, α : 4260 (3.24), 4010 (3.66); p: 3840 (4.52), 3640 (4.51); β : 3470 (4.62), 3220 (4.54); in benzene, β' : 2980 (4.74).

which has no possibility of cyclizing under the condition of the Elbs reaction, must involve migration of the o - toluyl group from the 5-position to the 6-position, the 6 - (o - toluyl) - 3.4, 9.10 - dibenzopyrene (XV) subsequently undergoing a normal Elbs cyclization. An analagous migration of an o - toluyl group is observed in the pyrolysis of 8 - (o - toluyl) - 1.2 - benzopyrene.[9]

EXPERIMENTAL

2 - (3' - Carboxy - 2' naphthoyl) - 1.4 - dimethylbenzene (XII).

An intimate mixture of finely powdered naphthalene - 2.3 - dicarboxylic anhydride (5g) and aluminium chloride (10g) was added to p - xylene (23g). The solution initially yellow became dark red orange and finally yellow-brown. When the initial vigorous reaction had ceased (10 min.) the mixture was heated at 80° for 1½ hours. The viscous yellow-brown complex was decomposed with dilute aqueous hydrochloric acid and after removal of the p - xylene by steam distillation the grey-white residue was extracted with ammonia and the filtered alkaline extract was acidified with concentrated hydrochloric acid. The white precipitate (7.4g) crystallized as white needles of 2 - (3' - carboxy - 2' - naphthoyl) - 1.4 - dimethylbenzene, m.p. 224 - 225°. The keto-acid dissolved in concentrated sulphuric acid to give a red solution which changed to

violet on standing.

Found: C, 79.3 ; H, 5.2.

$C_{20}H_{16}O_3$ requires: C, 78.95; H, 5.3%.

1.4 - Dimethyltetracene - 5.12 - quinone (XIII).

Powdered 2 - (3' - carboxy - 2' - naphthoyl) - 1.4 - dimethylbenzene (5g) was added to concentrated sulphuric acid (40g) and the mixture was heated at 100 - 110° with stirring, for 20 minutes. The initial red colour changed to violet. The mixture was poured onto ice and the precipitated yellow solid (4.41g) was washed with dilute ammonia and water. Crystallization of the yellow solid thus obtained from xylene furnished 1.4 - dimethyltetracene - 5.12 - quinone (XIII) as glistening yellow needles, m.p. 264 - 265°. The quinone dissolves violet in concentrated sulphuric acid.

Found: C, 84.0; H, 5.0.

$C_{20}H_{14}O_2$ requires: C, 83.9; H, 4.9%.

5.12 - Diphenyl - 5.12 - dihydroxy - 5.12 - dihydro - 1.4 - dimethyltetracene (XIV).

The above quinone (XIII) (5g) was added as a benzene slurry (150 ml) to an ethereal solution of phenyl lithium (prepared from lithium chips (1g) and bromobenzene (11g). The ether was distilled off and after refluxing for 15 minutes the complex was decomposed with ice and dilute

acetic acid. The benzene was steam distilled off and the resulting brown residue was dissolved in ether. After 2 days about 3g. of diol separated as a white crystalline powder. Crystallization from xylene gave 5.12 - diphenyl - 5.12 - dihydroxy - 5.12 - dihydro - 1.4 - dimethyltetracene as white needles, m.p. 260 - 290° dec. The diol gives a green colour in concentrated sulphuric acid.

Found: C, 86.8; H, 6.0.

$C_{32}H_{26}O_3$ requires: C, 86.9; H, 5.9%.

3.4, 9.10 - Dibenzo - naphtho - (2'''.3''' - 1.2) - Pyrene (II)

An intimate mixture of the above diol (XIV) (2.8g) and copper powder was pyrolysed in an atmosphere of carbon dioxide at 400° for 1½ hours. A yellow oil sublimed in the tube and this and the copper powder were extracted with boiling xylene. The xylene extract was chromatographed on alumina grade I with xylene as eluant. Two fractions were obtained, a yellow eluate followed closely by a bright red eluate. The yellow eluate was concentrated to small volume and pet. ether 60 - 80° added. On standing 3.4, 9.10 - dibenzo - naphtho (2'''.3''' - 1.2) - pyrene (259 mg) crystallized as long yellow needles, m.p. 274 - 276°. (II) dissolves in concentrated sulphuric acid to give a wine red solution.

Found: C, 95.6; H, 4.7.

$C_{32}H_{18}$ requires: C, 95.5; H, 4.5%.

Concentration of the bright red eluate gave no useful product.

5 - (o - Toluyl) - 3.4, 9.10 - dibenzopyrene (XVI).

Finely divided 3.4, 9.10 - dibenzopyrene (5g) was suspended in a solution of o - toluyl chloride (2.82g) in methylene chloride (30 ml). Powdered aluminium chloride (5g) was added in a single portion. A vigorous reaction occurred, hydrogen chloride was evolved and the initial blue colour of the solution changed to green. The mixture was shaken at room temperature for 5 minutes and then heated to boiling point for a few minutes. The complex was decomposed with dilute aqueous hydrochloric acid and the methylene chloride steam distilled off leaving a brown resin. A portion of the above resin was dissolved in xylene and chromatographed on alumina grade '0'. Two fractions were eluted with xylene. The first fraction on concentration yielded unchanged 3.4, 9.10 - dibenzopyrene. Concentration of the second fraction gave a yellow-brown oil which could not be crystallized.

4.5, 8.9 - Dibenzo - naphtho - (2'''.3''' - 1.2) - pyrene (I).

Crude 5 - (o - Toluyl) - 3.4, 9.10 - dibenzopyrene from the above Friedel - Crafts reaction was dissolved in xylene, the solution washed with ammonia, dried and the xylene distilled off. The residue was pyrolysed under the protection of carbon dioxide at 420° for 15 minutes and then briefly at 450°. The pyrolysate (4.5g) was sublimed in vacuo. Two sublimates were obtained, 3.4, 9.10 - dibenzopyrene (1g) and at a higher temperature a yellow-brown sublimate which was dissolved in a large volume of xylene and chromatographed on alumina grade I. A colourless eluate with a blue fluorescence was eluted with boiling

xylene. Eluting with hot 1.2.4. - trichlorobenzene gave in addition to a colourless eluate with a blue fluorescence a yellow eluate with a green fluorescence. Concentration of the combined xylene and trichlorobenzene colourless eluates gave 4.5, 8.9 - dibenzo - naphtho - (2'''.3''' - 1.2) - pyrene (12 mg) as golden brown needles. (I) softens at 400° melts at 404°, sublimes in small needles in vacuo and dissolves in concentrated sulphuric acid to give a brown solution.

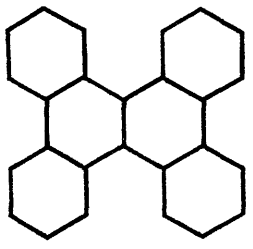
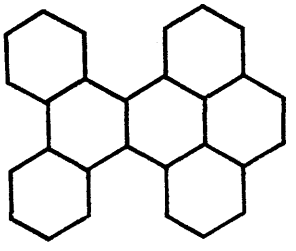
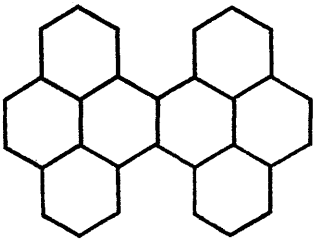
Found: C, 95.6; H, 4.45.

$C_{32}H_{18}$ requires: C, 95.5; H, 4.5%.

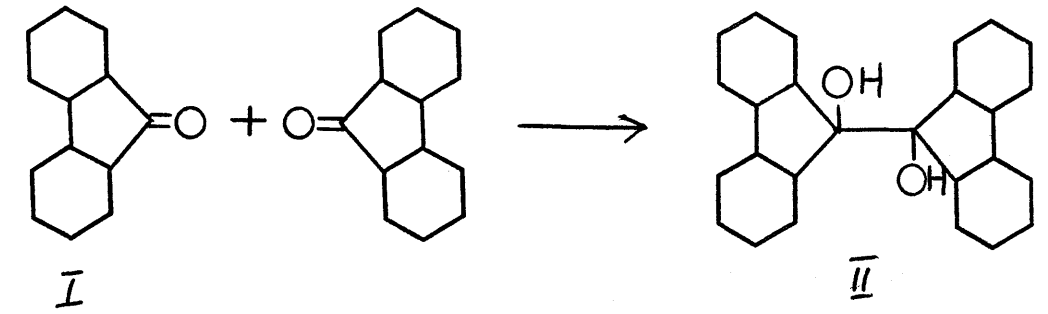
Concentration of the yellow trichlorobenzene eluate yielded a brown gum.

CHAPTER V.

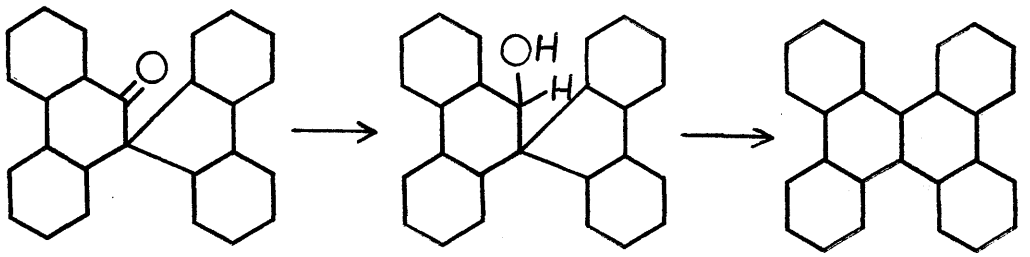
1.2, 7.8 - DIBENZOCHRYSENE, PYRENO - (1'.2' - 1.2) - PYRENE and PHENANTHRENO - (9'.10' - 1.2) - PYRENE.

INTRODUCTION: Several methods of obtaining 1.2, 7.8 - dibenzochrysene have been described in the literature. Pyrolytic methods are the pyrolysis of difluorenyl disulphide[1] and the pyrolysis of fluorene.[2] The more general route to 1.2, 7.8 - dibenzochrysene starts with fluorenone and is outlined in the reaction sequence I $\rightarrow$ V.



I II



III IV V

The reductive dimerization of fluorenone (I ⟶ II) has been carried out with zinc/mercury amalgam,[3] with magnesium/magnesium iodide[4] and electrolytically with magnesium electrodes.[5] 10.10 - Diphenylene - 9 - phenanthrone (III) has been obtained from (II) by pincol-pinacolone rearrangement[6] and directly from (I) by Clemmensøn reduction.[7,3] 1.2, 7.8 - Dibenzochrysene can be obtained from 10.10 - diphenylene - 9 - phenanthrone (III) by reducing (III) with hydriodic acid[8] or by Clemmensøn reduction.[3] Alternatively (III) is reduced to 10.10 - diphenylene - 9.10 - dihydro - 9 - phenanthrol (IV) with zinc and alcoholic ammonia[9] and this yields 1.2, 7.8 - dibenzochrysene (V) by retropinacolone rearrangement.[9,10,3]

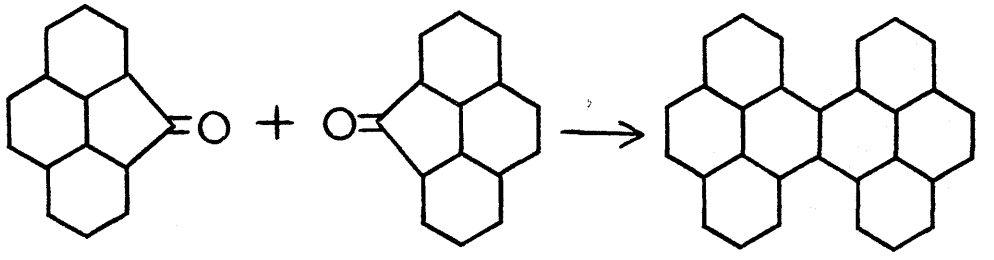
The Clar zinc dust melt[11] sometimes yields dimer products which

result from bimolecular condensations. For example, anthraquinone yields 9.9' - dianthryl while naphtho - (2'.7' - 1.8) - anthrone is reduced to a mixture of dinaphtho - (7'.1' - 1.13) (1''.7'' - 6.8) - peropyrene and dinaphtho - (7'.1' - 1.13) (1''.7'' - 9.11) - peropyrene.[12] Since fluorenone dimerizes readily on reduction and in view of the fact that the pyrolysis of fluorene gives 1.2, 7.8 - dibenzochrysene it was thought that a zinc dust melt on fluorenone would yield 1.2, 7.8 - dibenzochrysene.

EXPERIMENTAL DISCUSSION: When fluorenone was reduced in a zinc dust melt 10.10 - diphenylene - 9 - phenanthrone (III) was formed. This ketone was submitted to a second zinc dust melt and was partially converted to 1.2, 7.8 - dibenzochrysene (V). The resistance of 10.10 - diphenylene - 9 - phenanthrone to reduction under such vigorously reducing conditions is surprising but may be attributed to a purely physical property of the ketone - its low solubility in molten zinc chloride, the reducing medium. 10.10 - Diphenylene - 9 - phenanthrone (III) is the pinacolone of the 9.9' - dihydroxy - 9.9' - bifluorenyl (II) - 10.10 - diphenylene - 9 - phenanthrone pinacol-pinacolone system and hence during the first zinc dust melt dimerization I $\longrightarrow$ II and pinacol-pinacolone rearrangement II $\longrightarrow$ III have occurred. In the second melt 10.10 - diphenylene - 9 - phenanthrone is presumably reduced to 10.10 - diphenylene - 9.10 - dihydro - 9 - phenanthrol (IV) which is converted by retropinacolone

rearrangement to 1.2, 7.8 - dibenzochrysene.

Having obtained 1.2, 7.8 - dibenzochrysene by reducing fluorenone in a zinc dust melt it was decided to exploit this reaction and reduce 4.5 - carbonylphenanthrene[13] (VI) and a mixture of 4.5 - carbonylphenanthrene (VI) and fluorenone (I) respectively in a zinc dust melt.



VI VI VII

4.5 - Carbonylphenanthrene (VI) underwent smooth conversion to pyreno - (1'.2' - 1.2) - pyrene (VII). No trace of an intermediate "pinacolone" was found and the small amount of 4.5 - methylenephenanthrene which formed during the reduction was easily separated from crude pyrenopyrene by extraction with ethanol. Pyrenopyrene was purified by chromatography. The spectrum of (VII) is shown in Figure I.

A zinc dust melt of a mixture of 4.5 - carbonylphenanthrene (VI) and fluorenone (I) yielded three products, 10.10 diphenylene - 9 - phenanthrone (III), pyreno - (1'.2' - 1.2) - pyrene (VII) and phenanthreno - (9'.10' - 1.2) - pyrene (VIII).

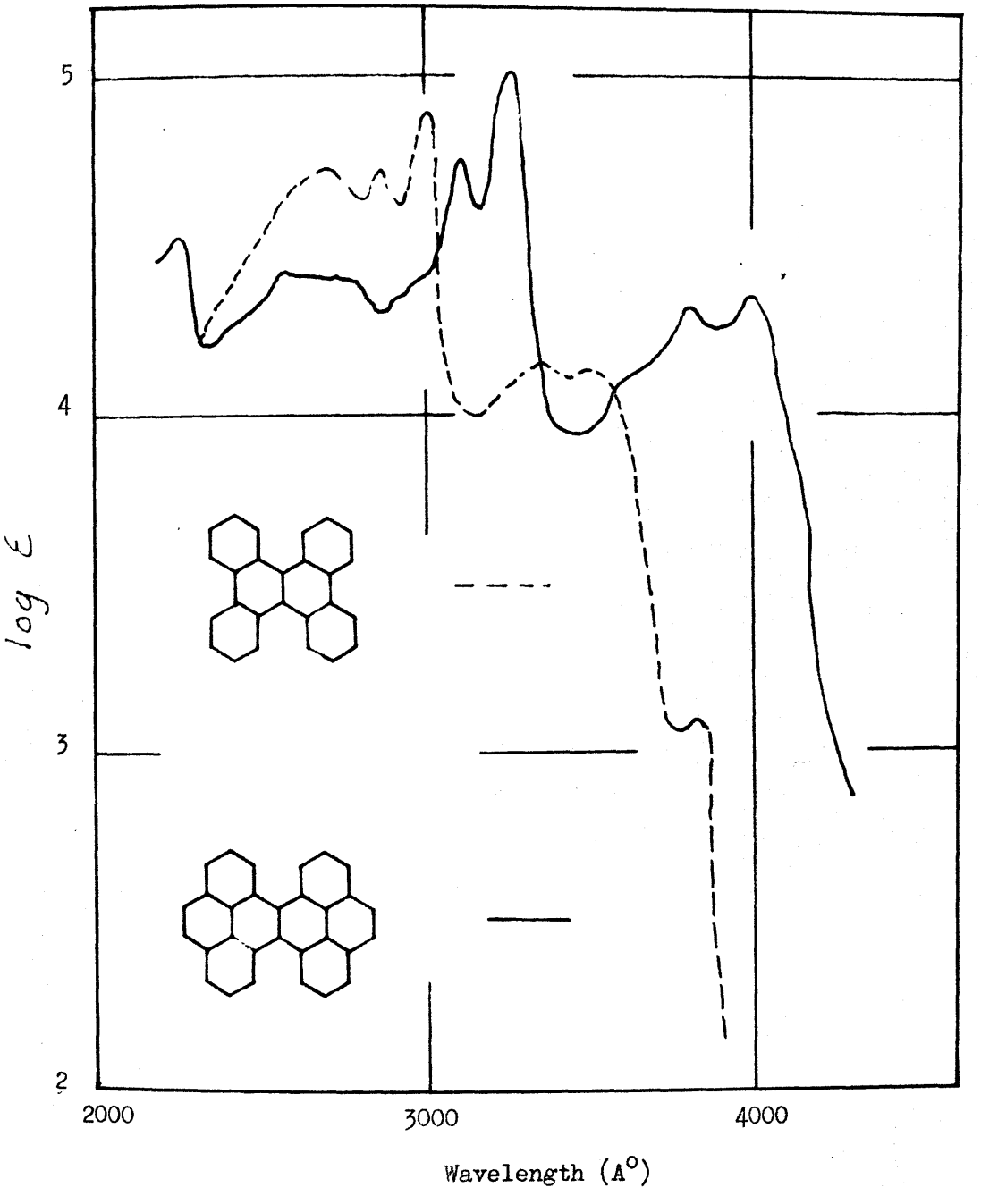
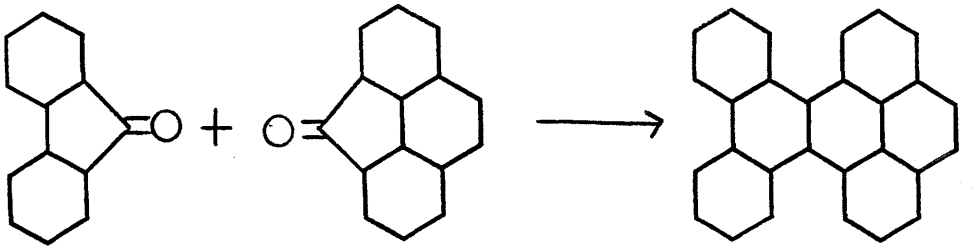


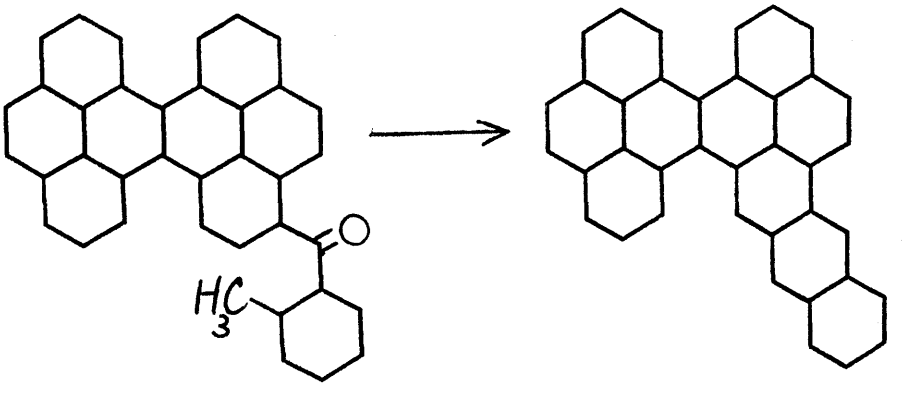
Figure 1. Absorption max. (A°) and log ε (in parentheses). 1.2, 7.8 - Dibenzochrysene in alcohol, α : 3830 (3.10); p: 3510 (4.14), 3360 (4.16); β : 3010 (4.90), 2880 (4.72); β': 2700 (4.72). Pyreno - (1'.2' - 1.2) - pyrene in cyclohexane, p: 4000 (4.34), 3800 (4.32); β : 3260 (5.01), 3100 (4.75); 2700 (4.40); 2260 (4.52).



I (VIII)

A separation of 10.10 - diphenylene - 9 - phenanthrone (III) from the two hydrocarbons was effected by chromatography on alumina with pet. ether 100 - 120° as solvent. A reasonable separation of pyreno - (1'.2' - 1.2) - pyrene and phenanthreno - (9'.10' - 1.2) - pyrene could not be achieved by chromatography and (VII) and (VIII) were separated by fractional crystallization from benzene. The spectrum of (VIII) is shown in Figure II.

o - Toluyl chloride, pyreno - (1'.2' - 1.2) - pyrene and aluminium chloride gave a uniform ketone 5 - (o - toluyl) - pyreno - (1'.2' - 1.2) - pyrene (IX).



(IX) (X)

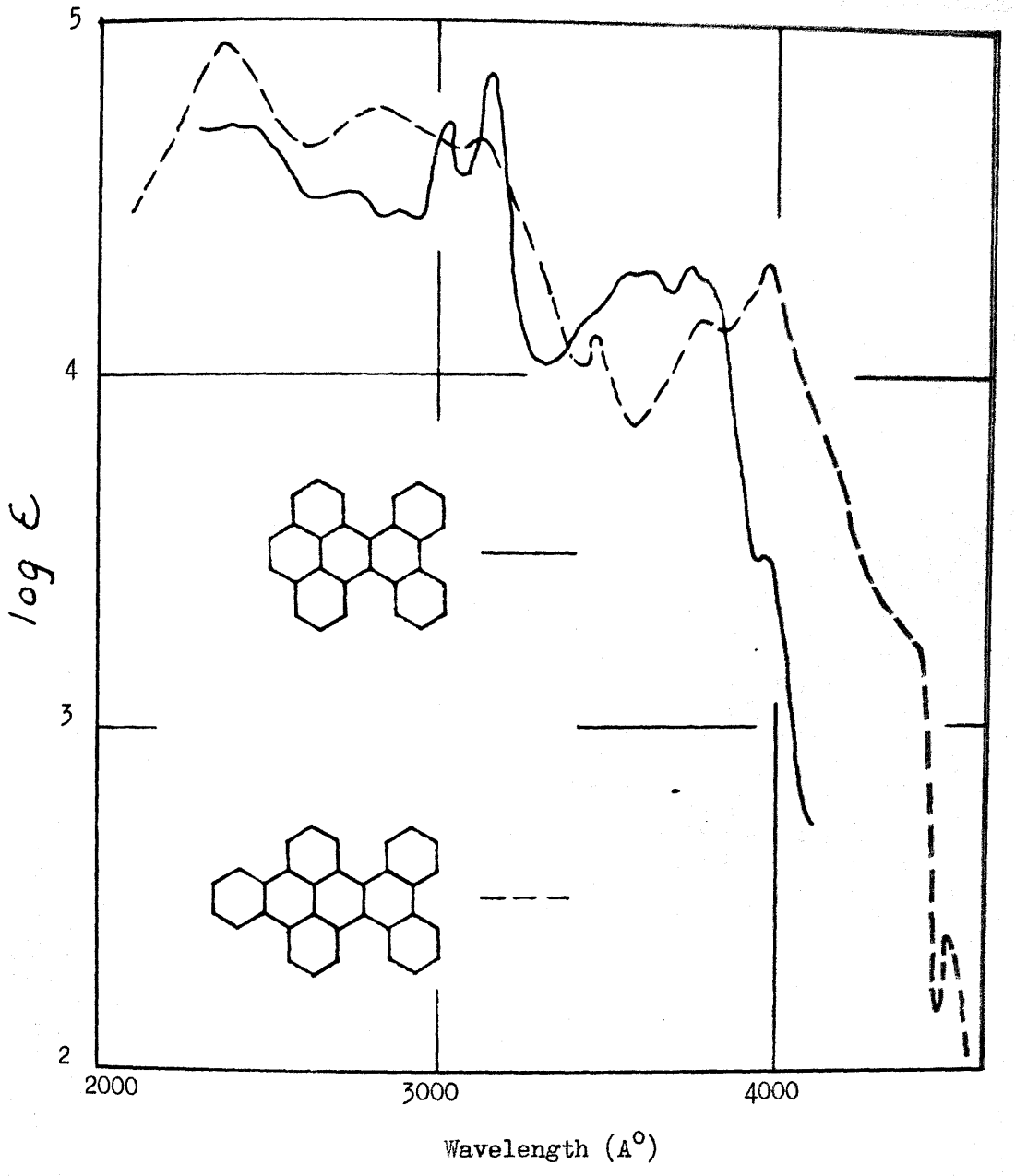


Figure 2. Absorption max. (A°) and log ε (in parentheses). Phenanthreno - (9'.10' - 1.2) - pyrene in cyclohexane, α : 3980 (3.45); p: 3740 (4.28), 3600 (4.26); β : 3140 (4.83), 3010 (4.68), 2900 (4.42); 2750 (4.48); 2480 (4.65), 2400 (4.65). 1.2 - Benzophenanthreno - (9'.10' - 6.7) - pyrene in benzene, α : 4540 (2.39), 4450 (3.24); p: 3980 (4.32), 3780 (4.15), 3450 (4.11); β : 3130 (4.65); in alcohol, 2800 (4.76); β': 2380 (4.94).

It is assumed that substitution occurs at the 5-position by analogy with pyrene which is substituted at the 3-position. The above ketone was pyrolysed at 420°. Extraction of the pyrolysate with xylene and chromatography of the xylene extract on alumina gave naphtho - (2''.3'' - 4.5) - pyreno - (1'.2' - 1.2) - pyrene (X) as orange-red needles. The spectra of pyrenopyrene and (X) are shown in Figure III.

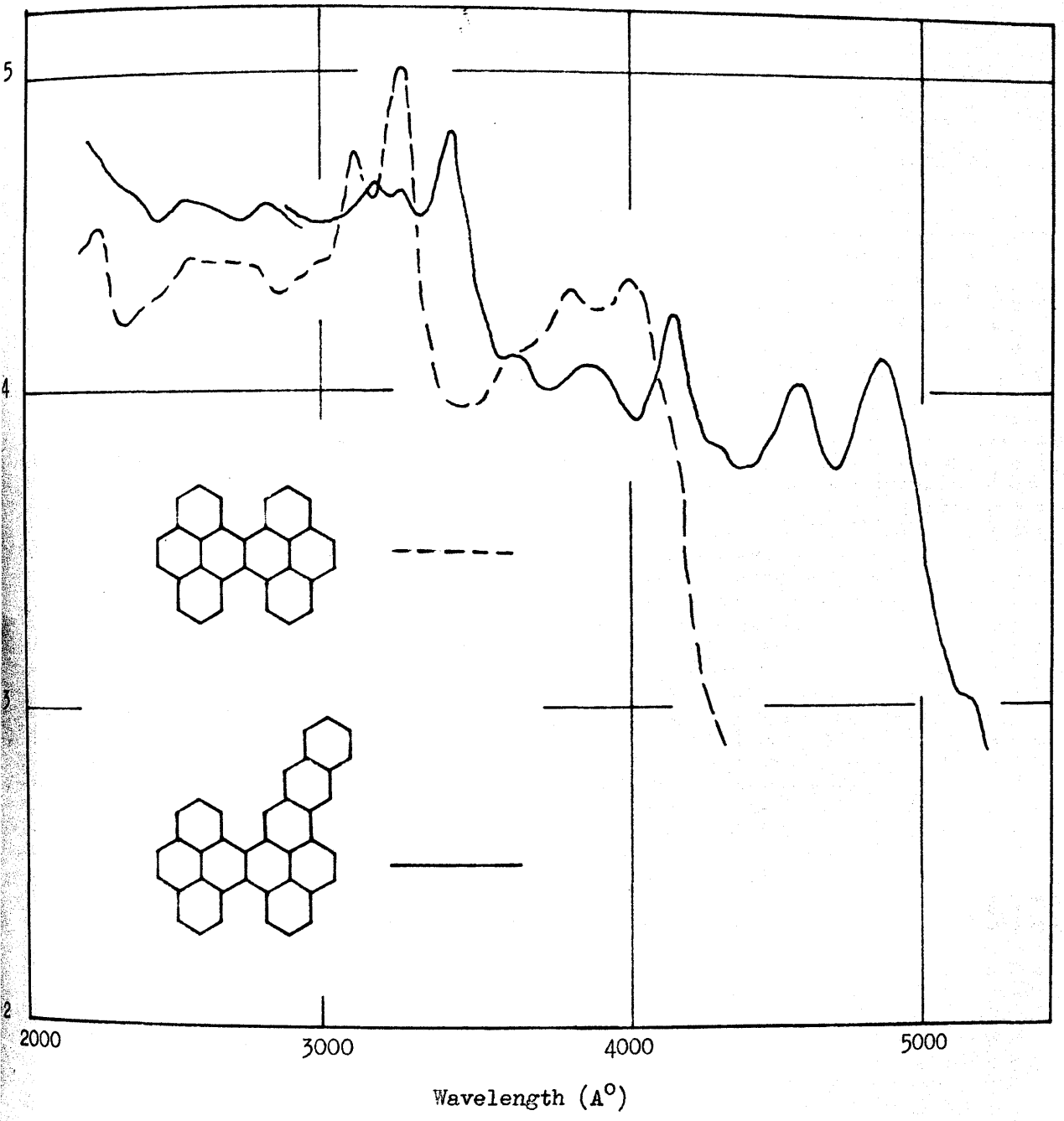
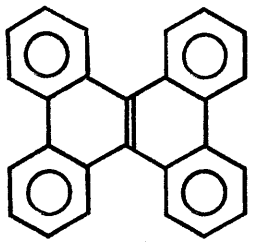
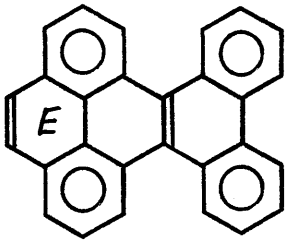


Figure 3. Absorption max. (A°) and log ε (in parentheses). Naphtho - (2''.3'' - 4.5) - pyreno - (1'.2' - 1.2) - pyrene in benzene, p: 4850 (4.10), 4560 (4.02); p': 4140 (4.24), 3850 (4.08), 3630 (4.10); β : 3420 (4.82), 3260 (4.63), 3170 (4.66); in cyclohexane, 2830 (4.60), 2570 (4.60). Pyreno - (1'.2' - 1.2) - pyrene as in Figure 1.

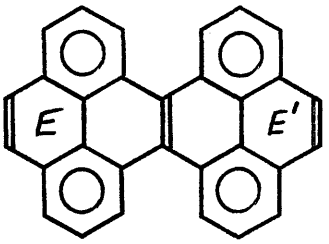
THEORETICAL DISCUSSION: 1.2, 7.8 - Dibenzochrysene (V) phenanthreno - (9'.10' - 1.2) - pyrene (VIII) and pyreno - (1'.2' - 1.2) - pyrene (VII) form an annellation series. A fourth member 1.2 - benzophenanthreno - (9'.10' - 6.7) - pyrene (XI) has recently been synthesised by A.D. Campbell.[14] Since the degree of overcrowding remains constant in the series no correction for overcrowding need be applied when comparing members within the series. The shifts observed in going from 1.2, 7.8 - dibenzochrysene (V) to phenanthreno - (9'.10' - 1.2) - pyrene (VIII) and from phenanthreno pyrene (VIII) to pyreno - (1'.2' - 1.2) - pyrene (VII) are 130 and 120 A° respectively for the β - bands.



V



VIII

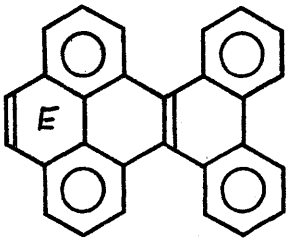


VII

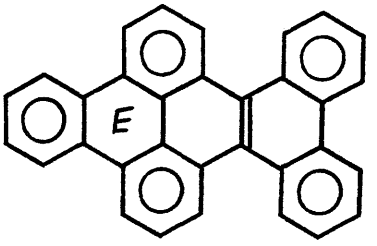
λ_β =	3010	+130 →	3140	+120 →	3260 A°
λ_p =	3510	+230 →	3740	+260 →	4000 A°

These shifts account for the formation of single bonds only and the newly formed rings E in phenanthrenopyrene (VIII) and E, E' in pyrenopyrene

(VII) must be empty. Building up 1.2 - benzophenanthreno - (9'.10' - 6.7) - pyrene (XI) (Figure II) from phenanthreno - (9'.10' - 1.2) - pyrene (VIII) by connecting a butadiene complex to the 6.7 double bond provides further support for the empty ring, E, in phenanthreno - (9'.10' - 1.2) - pyrene (VIII).



VIII



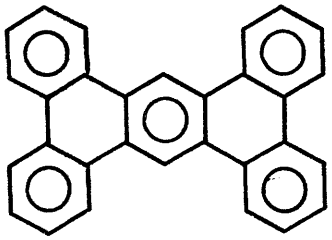
(XI)

λ_β = 3140 $\xrightarrow{-10}$ 3130 A°

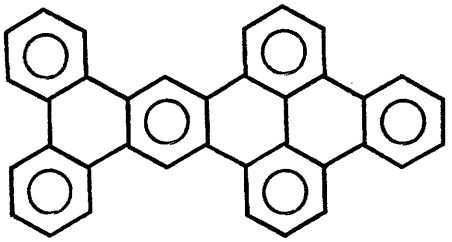
If the ring E in phenanthreno - (9'.10' - 1.2) - pyrene (VIII) is empty then the 6.7 double bond is a formally fixed double bond and connection of a butadiene complex to the 6.7 double bond should produce a small positive or negative shift.[15] The observed shift is in fact -10 A°.

Thus the series 1.2, 7.8 - dibenzochrysene (V), phenanthreno - (9'.10' - 1.2) - pyrene (VIII) and pyreno - (1'.2' - 1.2) - pyrene (VII) is a symmetric annellation series, a series in which a formally symmetric annellation is accompanied by a symmetric annellation effect. Another such symmetric annellation series is the series derived from 1.2, 3.4,

5.6, 7.8 - tetrabenzanthracene by the successive fusion of two o - phenylene complexes forming firstly tetrabenzopentacene,[16] (XIII) and tetrabenzo-heptacene[17] (XIV).

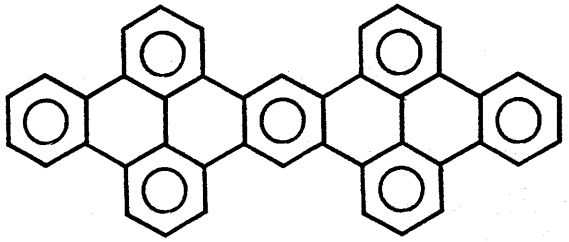


XII



XIII

λ_β = 2950 $\xrightarrow{+150}$ 3100



(XIV)

$\xrightarrow{+190}$ 3290 A°

A comparison of the spectra of naphtho - (2''.3'' - 4.5) - pyreno - (1'.2' - 1.2) - pyrene and pyreno - (1'.2' - 1.2) - pyrene (Figure III) shows that the short wavelength group of p - bands (p') can be related to the non-annellated pyrene complex and the long wavelength group (p) to the naphthopyrene complex in (X).

EXPERIMENTAL

10.10 - Diphenylene - 9 - phenanthrone (III).

Fluorenone (I) (20g) was ground together with zinc dust (20g) and sodium chloride (20g). Zinc chloride (100g) was added and the mixture was melted, the temperature being raised, with constant stirring to 320 - 330° for 4 minutes. The initial colour of the melt was green and this became bright red and dark red in turn, the dark red organic phase separating from the molten zinc chloride. The cold melt was decomposed with dilute acetic acid, and the residue was extracted with benzene. When the dark red extract was concentrated 10.10 - diphenylene - 9 - phenanthrone (III) (8.3g) crystallized from solution. The benzene mother liquor was chromatographed on alumina grade I. Eluting with pet. ether 100 - 120° gave a yellow eluate which yielded on concentration an additional 1.8 g of (III). Eluting with benzene gave a red eluate which on concentration

yielded a red resin. (III) crystallized from benzene in colourless prisms, m.p. 268 - 270° (lit. 258°).[8,9] The ketone dissolves in concentrated sulphuric acid to give an orange-yellow solution.

Found: C, 90.3; H, 4.8.
$C_{26}H_{16}O$ requires: C, 90.7; H, 4.7%.

1.2, 7.8 - Dibenzochrysene (V).

The above ketone (III) (2.5g) was ground together with zinc dust (2.5g), sodium chloride (2.5g) and moist zinc chloride (12.5g) were added. The mixture was melted and the temperature raised over 15 minutes to 320 - 330°. After the usual decomposition the grey residue was dissolved in benzene and the solution chromatographed on alumina grade I. Eluting with benzene gave two colourless fractions, the first having a strong blue fluorescence. Evaporation of the benzene from the first fraction and crystallization of the white solid thus obtained from acetic acid gave 1.2, 7.8 - dibenzochrysene (V) (200 mg) as long colourless needles, m.p. 218 - 220° (lit. 218°).[8,9] (V) dissolves slowly in concentrated sulphuric acid to give a colourless solution with a blue fluorescence.

Found: C, 95.1; H, 5.0.
$C_{26}H_{16}$ requires: C, 95.1; H, 4.9%.

Concentration of the second fraction yielded unchanged 10.10 - diphenylene - 9 - phenanthrone (III) (1.2g).

Pyreno - (1'.2' - 1.2) - pyrene (VII).

Sodium chloride (10g) and zinc chloride (50g) were added to an intimate mixture of 4.5 - carbonylphenanthrene (VI) (10g) and zinc dust (10g). The mixture was melted and the temperature raised, with stirring, to 320 - 330° for 4 minutes. The melt initially green in colour became red-brown. After decomposition of the cold melt with dilute acetic acid the residue was extracted with ethanol. Evaporation of the ethanol and crystallization of the residue from aqueous ethanol furnished 4.5 - methylenephenanthrene (500 mg) as colourless leaflets, m.p. 114 - 116° undepressed on admixture with an authentic sample of 4.5 - methylenephenanthrene. The ethanol insoluble residue was dissolved in xylene and chromatographed over alumina grade I. Eluting with hot xylene gave a yellow eluate with a violet-blue fluorescence, which on concentration gave pyreno - (1'.2' - 1.2) - pyrene (VII) (2.7g) as yellow leaflets, m.p. 302 - 304°. When allowed to crystallize slowly from xylene or benzene (VII) crystallizes in large thick yellow needles, m.p. 305 - 307°. (VII) dissolves in concentrated sulphuric acid slowly, the surface of the crystals becomes dark green and the solution yellow-green, the solution becoming dark green as the hydrocarbon dissolves.

Found: C, 95.8; H, 4.2.

$C_{30}H_{16}$ requires: C, 95.7; H, 4.3%.

Phenanthreno - (9'.10' - 1.2) - pyrene (VIII).

A mixture of 4.5 - carbonylphenanthrene (VI) (10g) and

fluorenone (I) (12g) was ground together with zinc dust (22g), sodium chloride (22g) and zinc chloride (110g). The mixture was melted and kept at 320 - 330° for 4 minutes. The colour changed from green to red-brown and the red-brown organic phase separated from the zinc chloride. After the usual decomposition with dilute acetic acid the residue was extracted with benzene and the extract chromatographed over alumina grade I. Eluting with pet. ether 100 - 120° and then with a 1:1 mixture of pet. ether 100 - 120° and benzene gave a yellow-brown eluate with a strong violet fluorescence followed by a colourless eluate from which 10.10 - diphenylene - 9 - phenanthrone (230 mg) was obtained on concentration. The combined pet. ether and pet. ether benzene fractions were rechromatographed on alumina with pet. ether 100 - 120° as eluant. The U.V. spectra of even the earliest fractions showed that pyreno - pyrene and phenanthreno - (9'.10' - 1.2) - pyrene were being eluted simultaneously. This chromatogram merely purified the mixture. The combined fractions from the second chromatogram were concentrated and the orange-yellow leaflets which crystallized from solution were dissolved in benzene. On standing pyreno - (1'.2' - 1.2) - pyrene (420 mg) crystallized out. The benzene mother liquor was concentrated when phenanthreno - (9'.10' - 1.2) - pyrene (VIII) (720 mg) m.p. 258 - 260° crystallized. After several crystallizations from benzene (VIII) crystallized in large pale orange prisms, m.p. 259 - 261°. (VIII) dissolves slowly in concentrated sulphuric acid to give a yellow-green changing to red-brown solution.

Found: C, 95.5 ; H, 4.7.

$C_{26}H_{16}$ requires: C, 95.45; H, 4.55%.

5 - (o - Toluyl) - pyreno - (1'.2' - 1.2) - pyrene (IX).

Finely powdered pyreno (1'.2' - 1.2) - pyrene (VII) (3g) was suspended in a solution of o - toluyl chloride (1.35g) in benzene (25 ml). Aluminium chloride (1.35g) was added - an intense blue coloured complex was formed immediately and hydrogen chloride was evolved. The mixture was heated on a water bath at 50° for 8 minutes and then at 60° for a further period of 15 minutes. The complex was decomposed with dilute hydrochloric acid and the benzene removed by steam distillation. The residue, after extraction with hot dilute aqueous ammonia was in the form of a yellow-brown resin (3.85g) which on treatment with ether gave a bright yellow amorphous powder. This was dissolved in benzene and chromatographed on alumina grade "O". Eluting with benzene gave a pale yellow eluate with a blue fluorescence (unchanged pyrenopyrene) followed by a yellow solution with a strong green fluorescence. The latter solution was concentrated to small volume and pet. ether 100 - 120° added. On standing clusters of small yellow needles of 5 - (o - toluyl) - pyreno - (1'.2' - 1.2) - pyrene (IX) crystallized from solution, m.p. 244 - 247°. (IX) was dissolved in benzene and rechromatographed on alumina grade "O". Concentration of the benzene eluate and addition of pet. ether 100 - 120° gave the ketone as small yellow needles, m.p. 253 - 254°. The ketone dissolves in concentrated sulphuric acid to give a blue-green solution which changes to claret red.

Found: C, 92.15; H, 4.5.

$C_{38}H_{22}O$ requires: C, 92.3 ; H, 4.5%.

Naphtho - (2''.3'' - 4.5) - pyreno - (1'.2' - 1.2) - pyrene (X).

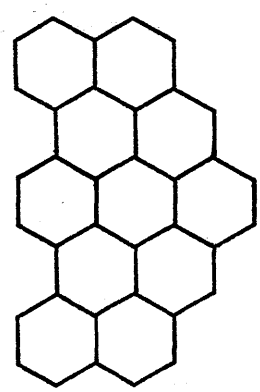
Crude ketone (IX) was dissolved in xylene, the solution filtered, the xylene distilled off and the residue heated at 430 - 440° under carbon dioxide. After about 10 minutes the elimination of water was complete and the pyrolysate (3.02g) was extracted with xylene and the xylene solution chromatographed on alumina grade I. Eluting with xylene gave firstly a yellow solution with a strong blue fluorescence which, on concentration, yielded leaflets of pyreno - (1'.2' - 1.2) - pyrene (200 mg), m.p. and mixed m.p. 302 - 304°. Secondly an orange-red eluate with a green fluorescence which afforded, on concentration, orange-red needles of naphtho - (2''.3'' - 4.5) - pyreno - (1'.2' - 1.2) - pyrene (170 mg). The hydrocarbon crystallized in rosettes of orange-red needles, m.p. 309 - 310°. It dissolves in concentrated sulphuric acid to give a violet solution which changes to green.

Found: C, 96.1; H, 4.2.

$C_{38}H_{20}$ requires: C, 95.8; H, 4.2%.

CHAPTER VI.

3.4, 5.6, 7.8, 12.13 - TETRABENZOPEROPYRENE.



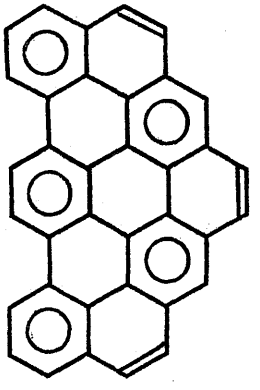
I

INTRODUCTION: 3.4, 5.6, 7.8, 12.13 - tetrabenzoperopyrene (I) was synthesised for spectral comparison with the isomeric 3.4, 5.6, 10.11, 12.13 - tetrabenzoperopyrene (II).[1]

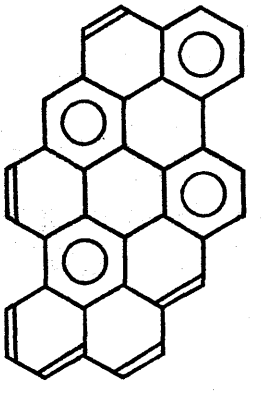
In addition it was thought possible that (I) would react with maleic

anhydride and open up a route to the hitherto unobtainable circo - phenanthrene.

THEORETICAL DISCUSSION: When written with the maximum number of aromatic sextets (marked with circles) 3.4, 5.6, 7.8, 12.13 - tetrabenzoperopyrene (I) has five inherent sextets while the isomeric 3.4, 5.6, 10.11, 12.13 - tetrabenzoperopyrene (II) has only four.



I



II

Isomer (I) therefore comes nearer to a fully benzenoid hydrocarbon like hexabenzocoronene[2] than (II). In consequence its para - bands are more shifted to the shortwave end of the spectrum than those of (II) (Figure I).

The annellation effects passing from 1.12, 2.3, 10.11 - tribenzoperylene[3] (III) to 3.4, 5.6, 7.8, 12.13 - tetrabenzoperopyrene (I) indicate that the system in aromatic conjugation in (I) is a triphenylene system. The shift observed in passing from (III) which contains the

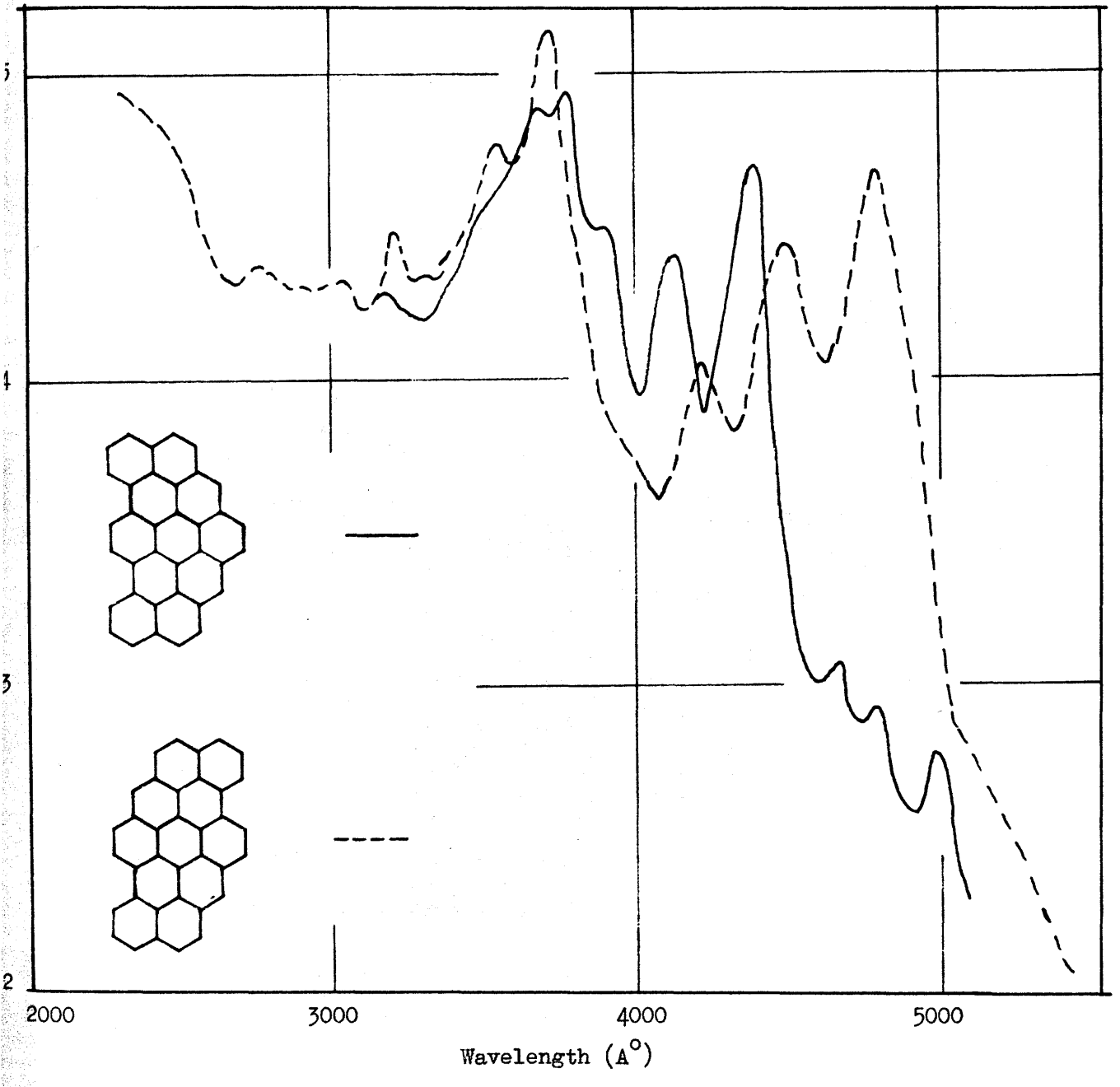
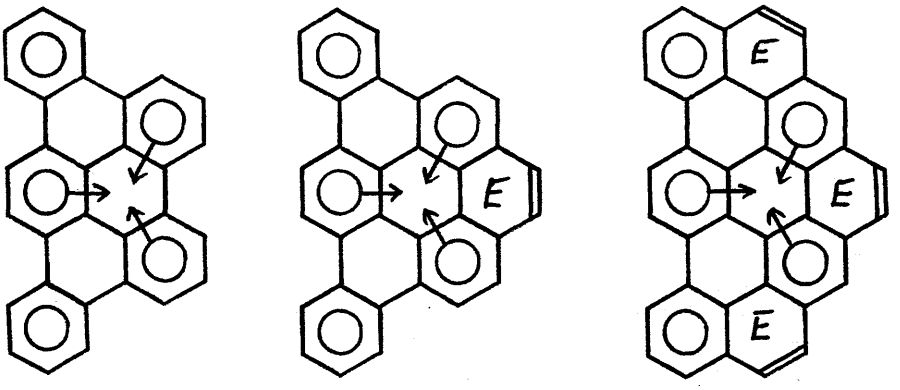


Figure 1. Absorption max. (A°) and log ε (in parentheses). 3.4, 5.6, 10.11, 12.13 - Tetrabenzoperopyrene in 1-methylnaphthalene, p: 4780 (4.66), 4490 (4.44), 4220 (4.04); β: 3710 (5.14), 3540 (4.76); in dioxane 3465 (4.78), 3200 (4.48), 3020 (4.32). 3.4, 5.6, 7.8, 12.13 - Tetrabenzoperopyrene in 1.2.4 - trichlorobenzene, α: 4980 (2.77), 4790 (2.92), 4660 (3.06); p: 4380 (4.68), 4120 (4.40); 3900 (4.49); β: 3780 (4.93); 3660 (4.88).

stable triphenylene complex to 1.2, 5.6 - dibenzocoronene[4] (IV) is small (260 A°) and accounts for the formation of the single bonds only and the newly formed ring in (IV) must be empty (E).



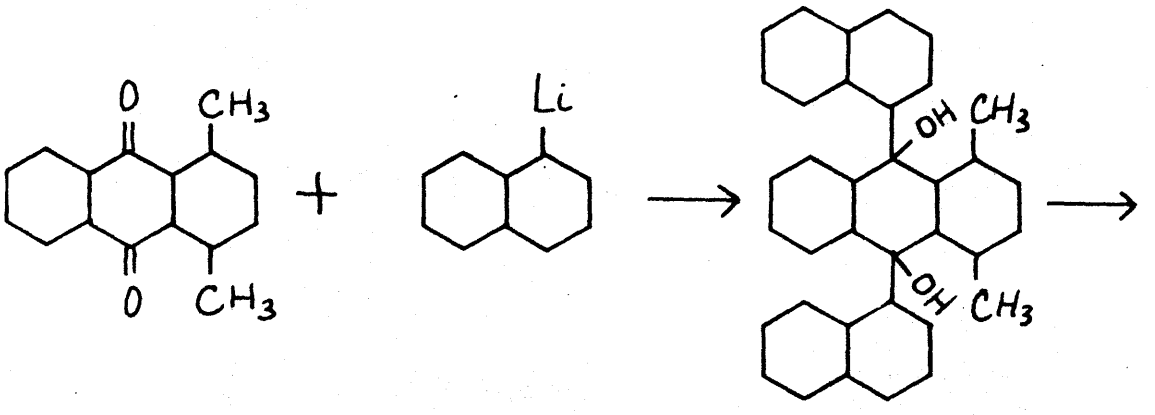
III IV I

λ_{β} = 3000 $\xrightarrow{+260}$ 3260 $\xrightarrow{+520}$ 3780 A°

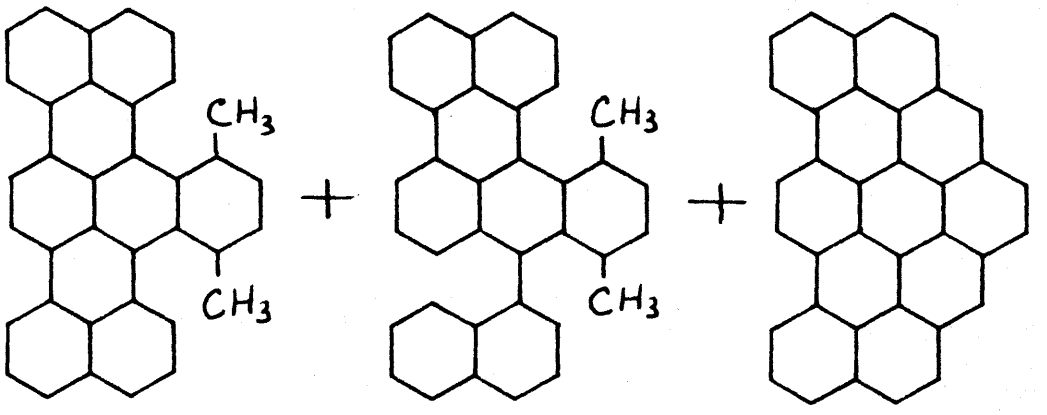
The annellation of two ethylene complexes to (IV) gives 3.4, 5.6, 7.8, 12.13 - tetrabenzoperopyrene (I) and is accompanied by a shift of 520 A°. This shift is well below the maximum value for four single bonds and hence the double annellation produces two empty rings and four single bonds.

EXPERIMENTAL DISCUSSION: 1.4 - Dimethylanthraquinone reacted with 1 - naphthyl lithium to give the diol (V) which was pyrolysed with copper powder at 400°. Sublimation of the pyrolysate in vacuo gave a green and a red hydrocarbon which sublimed together at the same temperature. Both hydrocarbons were extremely soluble in xylene and the solution of the hydrocarbons in xylene had two sets of absorption bands; λp, 6340, 5700 for the green hydrocarbon and λp, 5190, 4770 for the red hydrocarbon. The green and the red hydrocarbons are probably 1'.4' - dimethyl - 7.8 - benzoterrylene (VI) and 3 - naphthyl - (1) - 1'.4' - dimethyl - 1.2 - benzoperylene (VII) respectively, the parent hydrocarbons 7.8 - benzoterrylene and 1.2 - benzoperylene[5] have absorption bands λp, 6430, 5910, and λp5140, 4800 respectively. (VI) and (VII) obviously result from dehydration and partial dehydrogenation of the diol (V).

3.4, 5.6, 7.8, 12.13 - Tetrabenzoperopyrene (I), the major product of the pyrolysis sublimed at a higher temperature and was easily purified by sublimation in vacuo. (I) was insoluble in molten maleic anhydride and no adduct was formed after boiling for several hours.



V



VI VII I

EXPERIMENTAL

9.10 - Dinaphthyl - (1) - 9.10 - dihydroxy - 9.10 - dihydro - 1.4 - dimethylanthracene (V).

To a stirred solution of naphthyl lithium from lithium chips (2.7g) and 1 - bromonaphthalene (42g) in ether (100 ml) was added 1.4 - dimethylanthraquinone (10g) as a benzene slurry (250 ml). The ether was distilled off and the solution refluxed under nitrogen for 15 minutes. The dark brown complex which formed was decomposed with ice and dilute acetic acid. After removing the benzene by steam distillation the yellow-brown residue was triturated with ether - this resulted in the slow separation of (8g) of diol. When the ether mother liquor was allowed to stand for several days another (3.7g) of diol was obtained. Total yield (11.7g). The diol (V) crystallized from xylene in white needles, m.p. 268 - 270° dec.

Found: C, 88.0; H, 5.1.

$C_{36}H_{28}O_2$ requires: C, 87.8; H, 5.7%.

3.4, 5.6, 7.8, 12.13 - Tetrabenzoperopyrene (I).

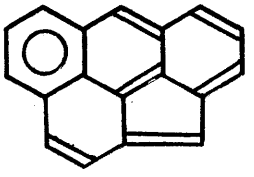
The above diol (4g) was ground with copper powder and pyrolysed under carbon dioxide at 400° for 3 hours. Sublimation of the pyrolysate in vacuo gave firstly a red and a green sublimate, both readily soluble in xylene. At a higher temperature 3.4, 5.6, 7.8, 12.13 - tetrabenzoperopyrene (370 mg) sublimed in fine orange-red needles. (I) was easily purified by subliming in vacuo and crystallized from 1.2.4 - trichlorobenzene in orange needles, m.p. 456°.

Found: C, 96.3; H, 3.8.

$C_{36}H_{16}$ requires: C, 96.4; H, 3.6%.

C H A P T E R VII.

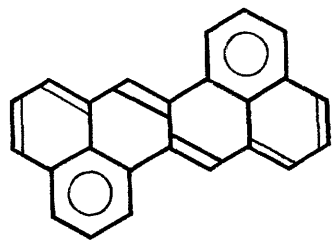
ATTEMPTED SYNTHESIS OF NAPHTHO - (7'.8' - 1.7) - ACENAPHTHYLENE.



I

INTRODUCTION: During the past decade molecules which have fixed double bonds have attracted much attention. Zethrene (II),[1] so called because of its Z shape may be taken as representative of this class of molecule. If only classical structures are used to describe zethrene then the two double bonds in the centre of the molecule are fixed. The adjacent naphthalene complexes can have

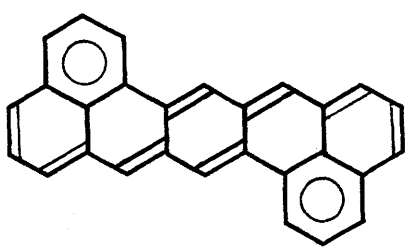
the same Kekule structures as naphthalene.



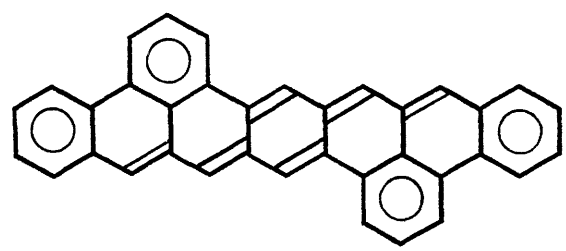
II.

Bond fixation does not deprive zethrene and its benzologues[2] of aromatic character and this is immediately obvious from the spectra of the zethrenes which are spectra typical of aromatic hydrocarbons.

Whereas zethrene and its benzologues have two fixed double bonds heptazethrene (III)[3] and dibenzoheptazethrene (IV)[4] have four and these take up a para quinonoid arrangement across the centre of the molecule.



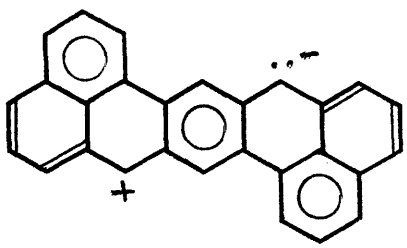
III.



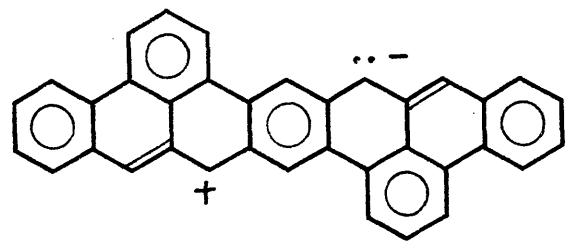
IV.

The most interesting feature of the heptazethrenes is their capacity for salt formation. These salts are probably derived from the polar forms

V and VI which contain no fixed double bonds.

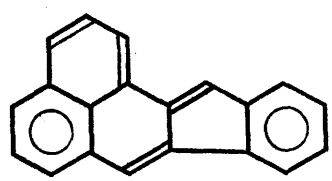


V



VI

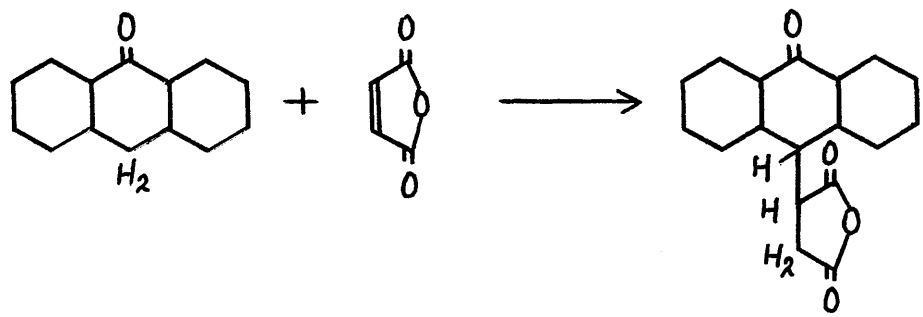
Bond fixation is not confined to hydrocarbons consisting exclusively of fused hexagonal rings and hydrocarbons with fixed double bonds are to be found among those hydrocarbons built up from six and five membered rings. One example is indeno - (2'.1' - 1.2) - perinaphthene (VII)[5] and like the heptazethrenes, (VII) is basic.



VII

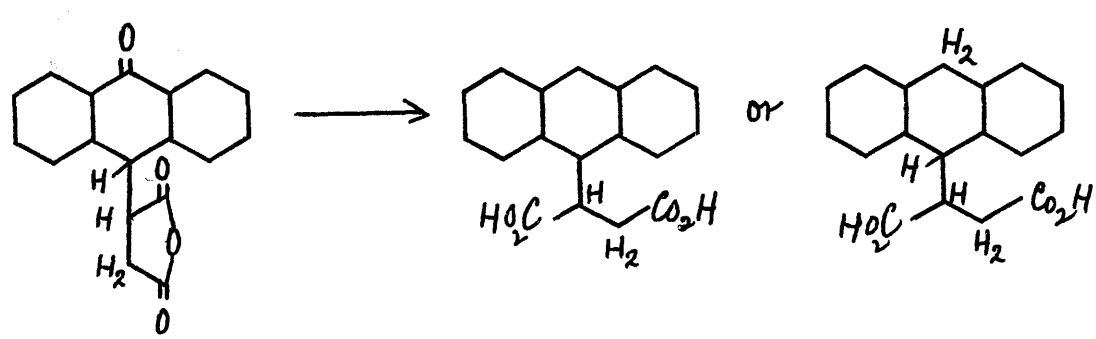
In the present chapter attempts to synthesise naphtho - (7'.8' - 1.7) - acenaphthylene (I) which has two fixed double bonds are described.

EXPERIMENTAL DISCUSSION: Molecular quantities of anthrone and maleic anhydride have been condensed to 10 - anthronylsuccinic anhydride in quantitative yield, in boiling p - tolyl ethyl ether. p - Tolyl ethyl ether was not available and the lower boiling phenyl ethyl ether was used as solvent for the condensation and the yield of (VIII) was somewhat lower.



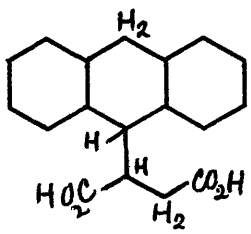
(VIII)

The reduction of 10 - anthronylsuccinic anhydride (VIII) to 9 - anthranyl-succinic acid (IX) and 9.10 - dihydro - 9 - anthranylsuccinic acid (X) with zinc and sodium hydroxide has been described in the literature.[6] Since conditions leading with certainty to either the aromatic acid (IX) or the dihydroaromatic acid (X) cannot be defined it was decided to aim for the dihydroaromatic acid (X).

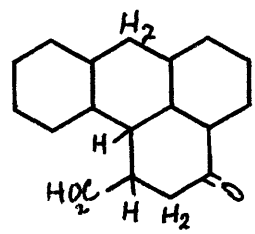


IX X

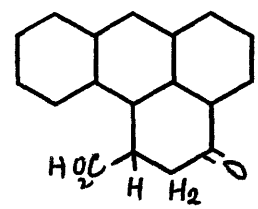
To ensure isolation of this acid in each experiment reduction was prolonged for 48 hours. The action of hydrofluoric acid on 9.10 - dihydro - 9 - anthranylsuccinic acid (X) did not furnish the expected cyclization product (XI) but gave (XII) which contains two hydrogen atoms less.



X

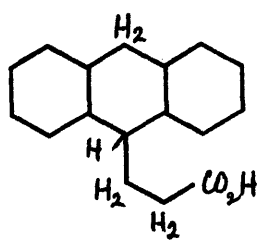


XI

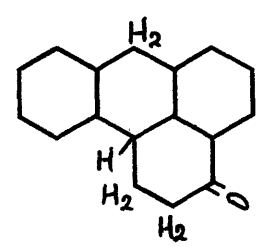


XII

In the analogous cyclization of the acid (XIII) to the cyclic ketone (XIV)[7] with hydrofluoric acid ring closure was accomplished without loss of hydrogen and the loss of hydrogen in our case is without an obvious explanation.



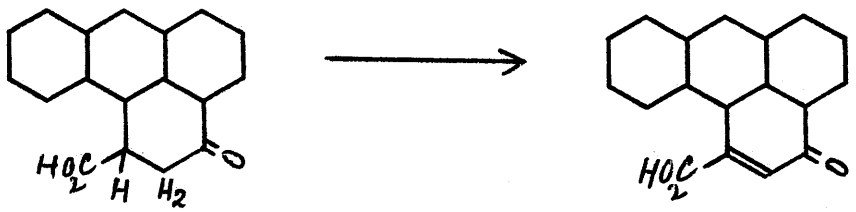
XIII



XIV

The yield for the ring closure was rather low and the large amount of red resinous material produced is perhaps in some way connected with dehydrogenation. The keto-acid (XII) was readily oxidised to benzanthrone -

(3) - 1 - carboxylic acid (XV) with selenium dioxide in acetic acid. (XII) even showed a tendency to oxidize when crystallized from o - dichlorobenzene or acetic acid.



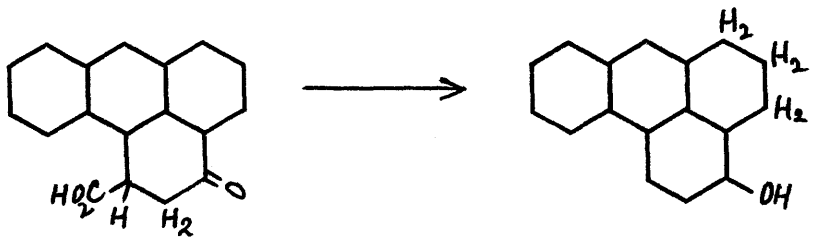
XV

Satisfactory analytical figures could not be obtained for (XV), a violet coloured compound which dissolved in concentrated hydrochloric acid to give a green salt.

When 1.2 - dihydro - benzanthrone - (3) - 1 - carboxylic acid (XII) was reduced with zinc and sodium hydroxide an ill defined readily oxidized compound which could not be crystallized was obtained. When this compound was submitted to a zinc chloride - sodium chloride melt at 320° 1.10 - trimethylenephenanthrene was formed. The reduction of (XII) by Clemmensøn reduction or with zinc and acetic acid gave no useful product.

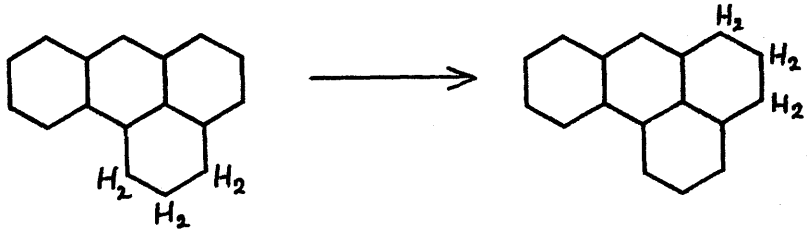
Reduction of (XII) with red phosphorus and hydriodic acid in a sealed tube at 160° gave a colourless crystalline compound, soluble in aqueous sodium hydroxide whose analytical figures and spectrum were consistent with its formulation as 2 - hydroxy - 1.10 - trimethylenephenanthrene (XVI). The spectra of 2 - hydroxy - 1.10 - trimethylenephenanthrene

and 9 - hydroxy - 1.10 - trimethylenephenanthrene[8] are shown in Figure I and the similarity between them is immediately apparent. Reduction has been attended by loss of carbon dioxide and isomerization.



XVI.

Isomerization is presumably motivated by the fact that a phenanthrene complex is more stable than an anthracene complex (the delocalisation energy of phenanthrene is 12 kcal greater than that of anthracene). A hypothetical 1.9 - trimethyleneanthracene will therefore isomerize to 1.10 - trimethylenephenanthrene.



When 1.2 - dihydro - benzanthrone - (3) - 1 - carboxylic acid (XII) was reduced with lithium aluminium hydride, sufficient to reduce both

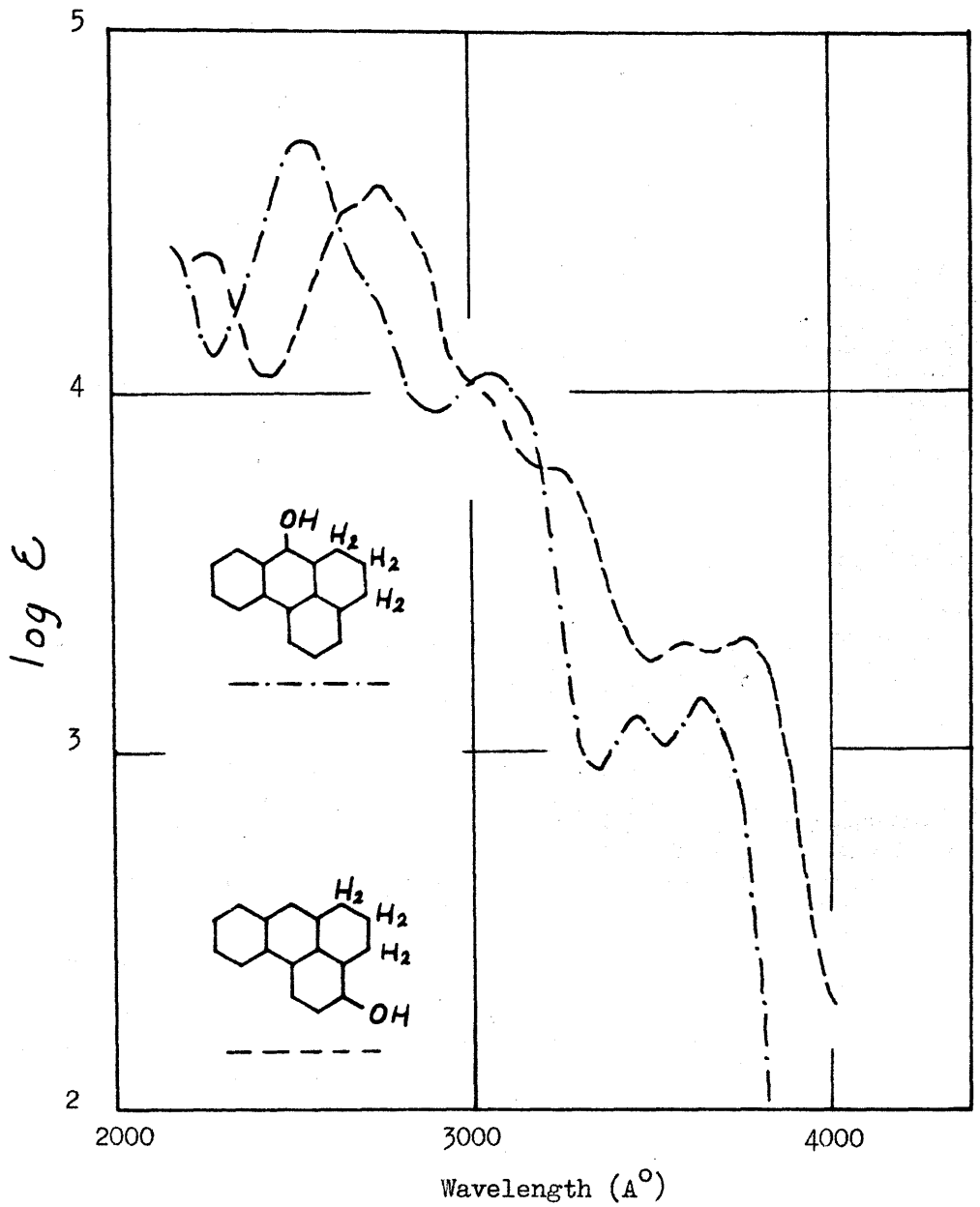
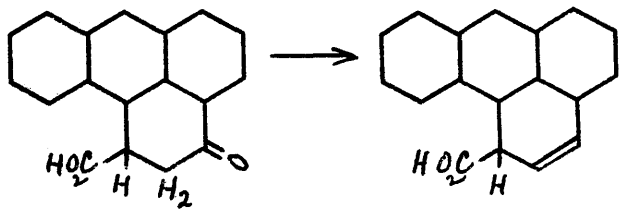
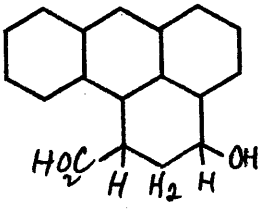


Figure 1. Absorption max. (A°) and log ε (in parentheses). 9 - Hydroxy - 1.10 - trimethylenephenanthrene, α : 3650 (3.15), 3480 (3.10); p: 3050 (4.05); β : 2550 (4.70). Potassium salt of 2-Hydroxy-1.10 - trimethylenephenanthrene in 50% alcohol/water, α: 3760 (3.31), 3600 (3.30); p: 3240 (3.79), 3040 (4.0); β : 2720 (4.58), 2290 (4.39).

carbonyl and carboxyl functions, 1H - benzanthrene - 1 - carboxylic acid (XVII) was obtained.

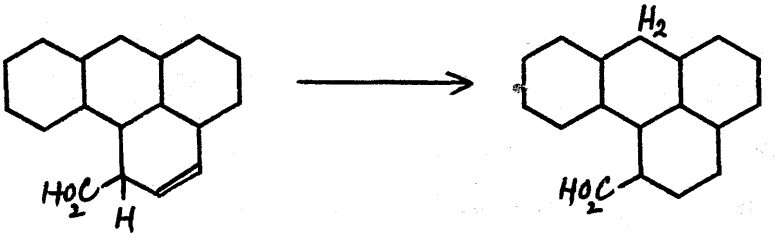


XVII



XVIII

The carboxyl group has not been reduced and no trace of the intermediate carbinol (XVIII) was found. This is presumably due to the presence of hydrochloric acid in the work up which causes a molecule of water to split out from (XVIII). 1H - Benzanthrene - 1 - carboxylic acid (XVII) was readily isomerized to 7H - benzanthrene - 1 - carboxylic acid (XIX) with hydrochloric acid.



XIX

This behaviour is analagous to the behaviour of 1H - benzanthrene [9] and 3H - benzanthrene[10] which are both readily isomerized to the more stable

7H - benzanthrene with hydrochloric acid. The spectra of 1H - benzanthrene - 1 - carboxylic acid and 1H - benzanthrene are shown in Figure II and the spectra of the isomeric 7H - benzanthrene - 1 - carboxylic acid and 7H - benzanthrene in Figure III. The spectrum of 1H - benzanthrene - 1 - carboxylic acid (XVII) is "anthracenoid" in character and exhibits the same fine structure as anthracene, a single β - band and a set of five para-bands. While the spectrum of Dannenberg's 1H - benzanthrene has absorption maxima at the same wavelength as the maxima in 1H - benzanthrene - 1 - carboxylic acid the bands at 374 (log ϵ 3.48) and 389 (log ϵ 2.64) do not fit into the anthracene pattern. The low intensity of the band at 389 (log ϵ 2.64) which has an intensity (log ϵ 3.93) in 1H - benzanthene - 1 - carboxylic acid suggests that Dannenberg's 1H - benzanthrene is impure.

7H - Benzanthrene is colourless and our 7H - benzanthrene - 1 - carboxylic acid is yellow. Although satisfactory analytical figures have been obtained for (XIX) it is obvious from a comparison of the spectra of (XIX) and 7H - benzanthrene that (XIX) is impure. This yellow impurity is conceivably benzanthrone - 1 - carboxylic acid formed by oxidation of (XIX).

With anhydrous hydrofluoric acid 1H - benzanthrene - 1 - carboxylic acid (XVII) yielded a black decomposition product.

A zinc dust melt on 1H - benzanthrene - 1 - carboxylic acid gave 4.5, 11.12 - dibenzoperopyrene (XX). The formation of (XX) from (XVII) requires the decarboxylation and dimerization of two molecules of (XVII). That such a dimerization which envolves the loss of hydrogen should take place under vigorously reducing conditions was most surprising

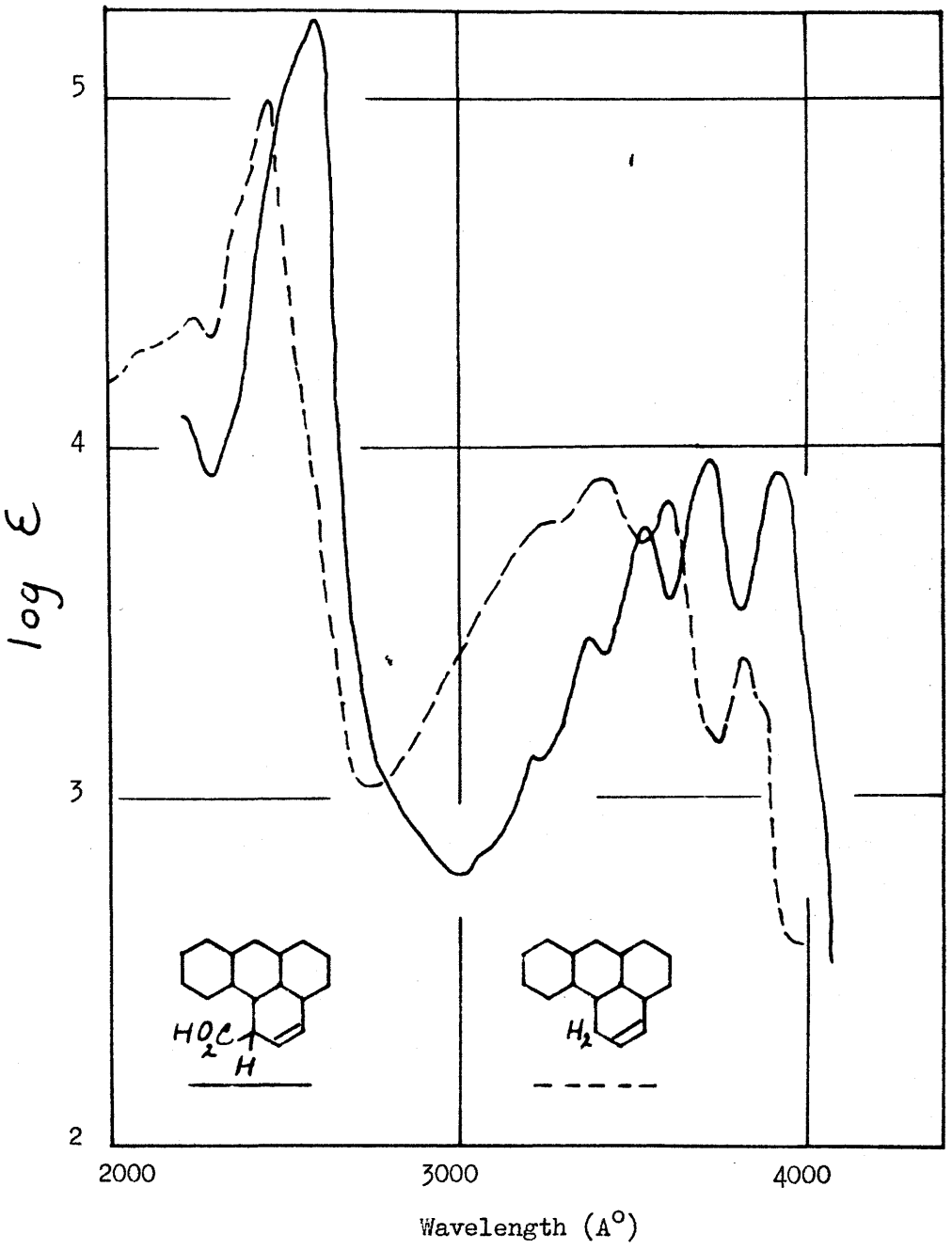
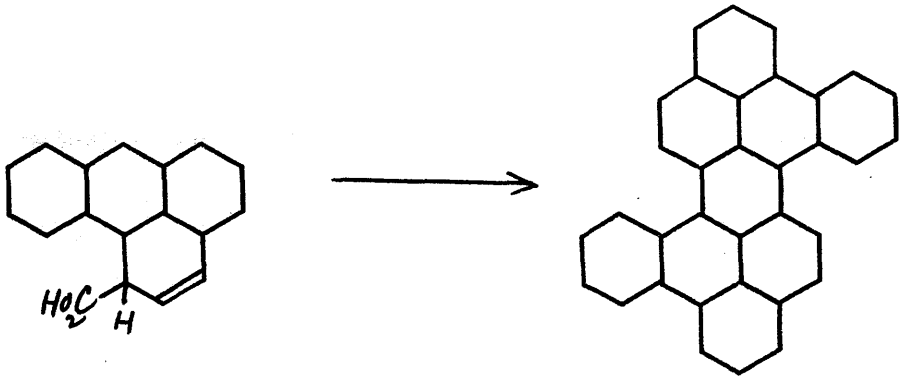


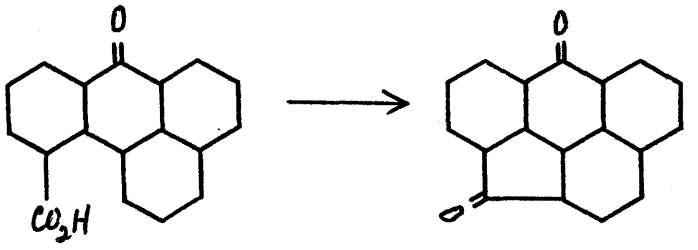
Figure 2. Absorption max. (A°) and log ε (in parentheses). 1H - Benzanthrene in alcohol, 3890 (2.64), 3740 (3.48), 3540 (3.90), 3370 (3.97), 3240 (3.81), 2510 (4.94), 2330 (4.37). Potassium salt of 1H - benzanthrene - 1 - carboxylic acid in 50% H_2O/alcohol, p: 3920 (3.93), 3720 (3.96), 3540 (3.77), 3380 (3.45), 3200 (3.12); β: 2590 (5.22).

and was totally unexpected.



XX

The two attempts to establish the naphtho - (7'.8' - 1.7) - acenaphthylene skeleton, firstly by melting the zinc/sodium hydroxide reduction product of (XII) with zinc chloride and secondly, by reducing 1H - benzanthrene - 1 - carboxylic acid in a zinc dust melt have been frustrated by the all too ready loss of carbon dioxide from these carboxylic acids. The naphtho - (7'.8' - 1.7) - acenaphthylene skeleton has been established by Bigelow and Rule[11] who obtained (XXII) by cyclizing the carboxylic acid (XXI) with phosphoric oxide in phthalic anhydride at 200°.



XXI XXII

If naphtho - (7'.8' - 1.7) - acenaphthylene is to be synthesised from 1H - benzanthrene - 1 - carboxylic acid then reduction of the carboxyl group to the hydroxymethylene group, before cyclization, is essential. Lack of material has prevented this course from being followed.

EXPERIMENTAL

10 - Anthronylsuccinic anhydride (VIII).

Anthrone (71.5g) and maleic anhydride (36g) in phenetole (250 ml) were heated under reflux for 3 hours. On cooling brown-white crystals of 10 - anthronylsuccinic anhydride (82g), m.p. 214 - 218° (lit. 215°)[6] separated.

9.10 - Dihydro - 9 - anthranylsuccinic acid (X).

10 - Anthronylsuccinic anhydride (57g) was dissolved in boiling sodium hydroxide solution (5%, 1300 ml) and zinc dust (168g) added in portions over 48 hours. The initial deep red colour changed to yellow. The hot solution was filtered from excess zinc which was washed with hot water and the filtrate was acidified with concentrated hydrochloric acid. Crystallization of the resin thus obtained furnished

9.10 - dihydro - 9 - anthranylsuccinic acid (17g) as small white prisms, m.p. 210 - 211° (lit. 211°)[6]. (X) dissolved in concentrated sulphuric acid to give a pale yellow solution.

1.2 - Dihydro - benzanthrone - (3) - 1 - carboxylic acid (XII).

9.10 - Dihydro - 9 - anthranylsuccinic acid (20g) was added to anhydrous hydrofluoric acid (500 ml) in a polythene vessel. The acid dissolved on stirring to give a yellow solution. Excess reagent was allowed to evaporate overnight and the resulting deep red solution was poured onto ice. The bright yellow cyclization product was collected by suction filtration and washed thoroughly with cold and warm water. During the course of the washing the yellow cyclization product turned red and became resinous. The resin dissolved in hot xylene and on standing 1.2 - dihydro - benzanthrone - (3) - 1 - carboxylic acid (6g) crystallized from solution in yellow brown needles. A second crystallization from xylene gave (XII) as clusters of golden yellow needles, m.p. 236 - 238° which dissolve in concentrated sulphuric acid to give a blue solution which changes to red on standing. Evaporation of the xylene gave a red-brown resin.

Found: C, 78.3; H, 4.3.

$C_{18}H_{12}O_3$ requires: C, 78.2; H, 4.4%.

Benzanthrone - (3) -1- carboxylic acid (XV).

1.2 - Dihydro - benzanthrone - (3) - 1 - carboxylic acid

(500 mg) was dissolved in glacial acetic acid (30 ml) selenium dioxide (200 mg) was added and the mixture was heated under reflux for 2 hours. The violet oxidation product which had precipitated out during the course of the oxidation was filtered off and extracted with dilute aqueous ammonia. Acidification of the filtered alkaline extract with concentrated hydrochloric acid gave benzanthrone - (3) - 1 - carboxylic acid (200 mg) as a violet powder, m.p. 238 - 238° dec. (XV) could not be crystallized and a sample purified by precipitation from ammonia did not give satisfactory analytical figures. (XV) dissolves in concentrated sulphuric acid to give a green solution with a red fluorescence. (XV) also dissolves in concentrated hydrochloric acid to give a green solution, dilution of this solution with water precipitates the violet benzanthrone - (3) - 1 - carboxylic acid (XV).

Found: C, 76.9; H, 3.4.

$C_{18}H_{10}O_3$ requires: C, 78.8; H, 3.7%.

1.10 - Trimethylenephenanthrene.

Crude cyclization product from 9.10 - dihydro - 9 - anthranyl-succinic acid (20g) was reduced by refluxing from zinc dust (60g) and dilute sodium hydroxide (5%, 500 ml) for 48 hours. The initial orange-yellow colour of the solution faded to pale yellow and acidification of the filtered alkaline solution with concentrated hydrochloric acid gave a yellow precipitate. On exposure to air this product rapidly became pink. The crude reduction product (7.5g) was ground together with zinc chloride

(37.5g) and sodium chloride (7.5g). The mixture was melted and the temperature raised, with stirring, to 300° for 4 minutes. The melt at first green in colour became brown-red. The cold melt was digested with dilute acetic acid and the residue extracted with xylene and the xylene extract chromatographed on alumina grade I. Eluting with benzene gave several fractions. Firstly a yellow eluate with a violet fluorescence which on concentration yielded a yellow-red oil. This distilled in vacuo (water pump) at 360° to give a pale yellow distillate which crystallized in pale yellow needles. After a washing with pet. ether 100 - 120° the needles had, m.p. 74 - 76°. Crystallization from ethanol (Charcoal) gave 1.10 - trimethylenephenanthrene (500 mg) as colourless needles, m.p. 78 - 79°, mixed m.p. with an authentic sample 79 - 80°. Later fractions, yellow with a green fluorescence, yielded no useful product on concentration.

2 - Hydroxy - 1.10 - trimethylenephenanthrene (XVI).

1.2 - Dihydro - benzanthrone - (3) - 1 - carboxylic acid (1g) red phosphorus (450 mg) and 45% hydriodic acid (2.5 ml) were heated in a sealed tube at 160° for 12 hours. Water was added and the solid material filtered off and extracted with 2N sodium hydroxide containing a little sodium sulphite. The alkaline solution was filtered from the unused phosphorus and acidified with concentrated hydrochloric acid. The pink precipitate (260 mg) crystallized from benzene in colourless needles (made violet by a violet colour impurity) of 2 - hydroxy - 1.10 - trimethylenephenanthrene, m.p. 206 - 208°.

Found: C, 87.0; H, 5.9.

$C_{17}H_{14}O$ requires: C, 87.1; H, 6.0%.

1 H - Benzanthrene - 1 - carboxylic acid (XVII).

1.2 - Dihydro - benzanthrone - (3) - 1 - carboxylic acid (7.85g) in dry tetrahydrofuran (197 ml) was added during 45 minutes to a stirred suspension of lithium aluminium hydride (1.73g) in tetrahydrofuran (118 ml) in an atmosphere of nitrogen. When the addition was complete the mixture was stirred for a further 30 minutes, cooled in ice and excess hydride destroyed by the cautious addition of water. The mixture was acidified with 20% aqueous hydrochloric acid and the organic phase extracted with ether. The ethereal layer was separated and extracted with 5% sodium hydroxide. The alkaline extract was separated from the ether and acidified with concentrated hydrochloric acid. The oily precipitate which formed solidified on boiling to give 1H - benzanthrene - 1 - carboxylic acid (4.02g) as a dirty white powder. (XVII) crystallized from acetic acid in fine colourless needles, m.p. 220 - 222° which dissolve readily in sulphuric acid to give a red solution with a red fluorescence.

Found: C, 83.3 ; H, 4.9.

$C_{18}H_{12}O_2$ requires: C, 83.05; H, 4.65%.

The ethereal layer was evaporated to dryness and the dark red resinous product (3.4g) which was obtained could not be crystallized. It gave a red colour with concentrated sulphuric acid.

7H - Benzanthrene - 1 - carboxylic acid (XIX).

The above acid (XVII) (100 mg) was dissolved in acetic acid (5 ml) and a drop of concentrated hydrochloric acid added. The solution was refluxed for 5 minutes and the acetic acid was then distilled off. The resulting yellow solid, m.p. 170 - 174° was crystallized from xylene and after repeated crystallization gave 7H - benzanthrene - 1 - carboxylic acid (30 mg) as yellow needles, m.p. 178 - 180°. (XIX) dissolves in concentrated sulphuric acid red with a red fluorescence.

Found: C, 82.8 ; H, 4.8.

$C_{18}H_{12}O_2$ requires: C, 83.05; H, 4.65%.

Zinc dust melt on 1H - benzanthrene - 1 - carboxylic acid (XVII).

1H - Benzanthrene - 1 - carboxylic acid (4.02g) was ground together with zinc dust (4.02g) and sodium chloride (4.02g). Zinc chloride (20.1g) was added and the mixture heated, with stirring, to 320° for 3 minutes. The cold melt was digested with dilute acetic acid and the zinc dust was destroyed with concentrated hydrochloric acid. The brown residue was extracted with xylene and the xylene extract chromatographed on alumina grade I. Eluting with benzene gave an orange-yellow eluate which yielded on concentration thick orange-red needles of 4.5, 11.12 - dibenzoperopyrene (XX) (80 mg), m.p. and mixed m.p. with an authentic sample 346 - 347°. Evaporation of the benzene mother liquor gave a brown gum.

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